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Luminescence and Resonance Raman Study of Molecular Distortions Caused by Ligand-Centered Transitions in Metal Acetylacetonate Complexes

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Introduction

The utility of metal β-diketonate complexes as precursors for the thermal and photochemical production of metal films via metal organic chemical vapor deposition (MOCVD) has stimulated an interest in the electronic properties of these complexes.[1−5] In a recent study of the laser-assisted MOCVD of pure gold by irradiating dimethylgold(III) hexafluoroacetylacetonate [$Me_2Au(hfac)$] in the gas phase, it was shown that the molecule fragments to produce bare atoms and dimers.[1] In condensed media, however, the molecule luminesces, and the low temperature emission spectrum contains highly resolved vibronic structure.[6] Reports of both the emission spectra and the assignments of such spectra of metal β-diketonate complexes are sparse.[7−9]

The studies reported in this paper have dual purposes. The first is to examine the emission spectra of acac and substituted acac complexes of metals with filled shells for comparison with the spectra of the gold complexes in order to investigate the proposed assignment of the transition as π to π^* ligand-centered luminescence. The second purpose is to use the resolved vibronic structure, if any, to determine which normal modes undergo distortions as a result of the transition and thus be able to infer which orbitals are involved. This knowledge can also assist in assigning the spectra. In this paper we report the emission spectra of $Zn(hfac)_2{\cdot}2H_2O$, $Me_2Au(tfac)$, $Me_2Au(acac)$, and $Al(acac)_3$ at low temperature. The spectrum of $Zn(hfac)_2{\cdot}2H_2O$ contains the best resolved structure, and this spectrum is analyzed in detail by using a combination of resonance Raman spectroscopy and time-dependent theory. The spectra of the compounds are compared and used to support the assignment of the emissions as π to π^* ligand-centered transitions.

Experimental Section

Spectra. The low temperature emission spectra were taken at 18 K using an Air Products displex closed-cycle refrigeration system for cooling. The excitation wavelength was 308 nm from an XeCl excimer laser. The emitted light was collected, passed through a 0.32 m ISA monochromator with a 300 grooves/mm grating, and then detected with an EG&G OMA3 diode array detector. The resonance Raman spectrum of solid $Zn(hfac)_2{\cdot}2H_2O$ at room temperature was measured using the 350.7 nm line from a Kr^+ ion laser and an ISA triple monochromator with CCD detection (Princeton Instruments 1024 EUV). All of the spectra were corrected for instrument response.

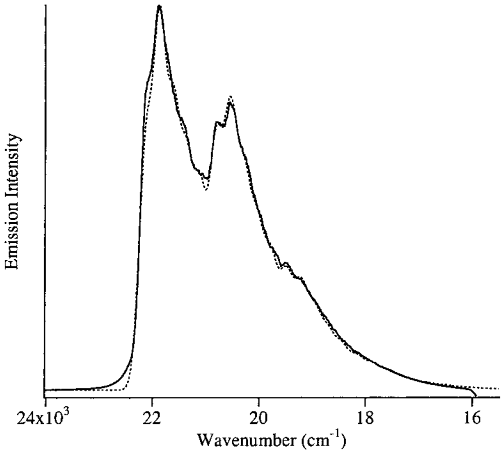

Figure 1. Comparison of the calculated (broken lines) and experimental (solid lines) emission spectrum of $Zn(hfac)_2{\cdot}2H_2O$.

Theory

The vibronic structure in the emission spectra is analyzed by using the time dependent theory of electronic spectroscopy. Because the theory has been extensively discussed,[10−15] only the relevant equations will be presented here. The time-dependent overlap is

$$|\langle\phi_k|\phi_k(t)\rangle| = \exp\left\{-\frac{1}{2}\Delta_k^{\,2}(1 - e^{-i\omega_k t}) - \frac{i\omega_k t}{2}\right\} \qquad (1)$$

where Δ_k is the dimensionless distortion of the first excited state along the kth normal mode and ω_k is its vibrational frequency. The total overlap is the product of the overlap functions for each mode:[10−12]

$$\langle\phi|\phi(t)\rangle = \prod_k \langle\phi_k|\phi_k(t)\rangle \qquad (2)$$

The emission spectrum is the Fourier transform of the overlap function[10−12]

$$I(\omega) = C\omega^3\int_{-\infty}^{+\infty}\exp(i\omega t)\left\{\langle\phi|\phi(t)\rangle\exp\left(-\Gamma^2t^2 + \frac{iE_{00}}{\hbar t}\right)\right\}\mathrm{d}t \qquad (3)$$

where C is a constant, $I(\omega)$ is the intensity on photons per unit volume per unit time at frequency ω, E_{00} is the electronic shift in energy between the minima of the excited and ground state potential surfaces, and Γ is the damping factor.

Results

Emission Spectra. The emission spectra of solid samples of $Zn(hfac)_2{\cdot}2H_2O$, $Me_2Au(tfac)$, $Me_2Au(acac)$, and $Al(acac)_3$ measured at 18 K and excited at 308 nm are shown in Figures 1 and 2. The emission spectra of the two non-fluorinated acetylacetonate compounds have similar onset energies of 25 000 cm^{-1}. The full width at half-maximum (fwhm) of the two bands are also very similar (~3500 cm^{-1}). The spectrum

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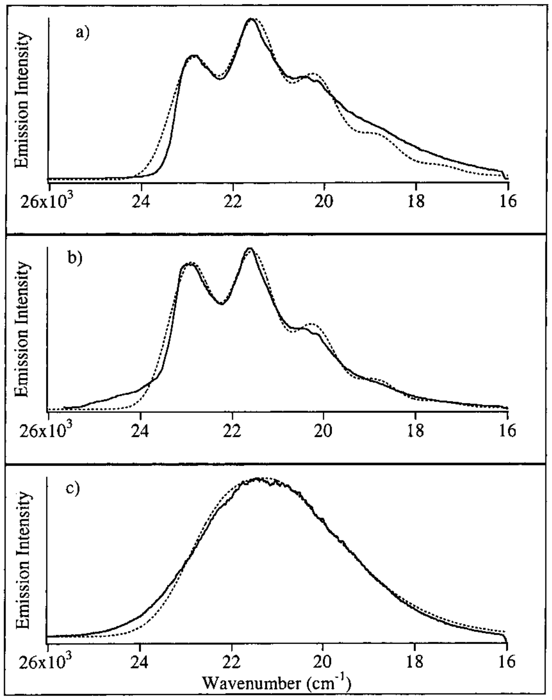

Figure 2. Comparison of the calculated (broken lines) and experimental (solid lines) emission spectra of (a) $Me_2Au(tfac)$, (b) $Me_2Au(acac)$, and (c) $Al(acac)_3$.

of $Al(acac)_3$ consists of a single broad band whereas that of the $Me_2Au(acac)$ compound contains resolved vibronic structure with the main progression consisting of a spacing of about 1350 cm^{-1}.

The emission spectrum of $Me_2Au(tfac)$ has an E_{00} of about 23 000 cm^{-1} and a fwhm of about 4000 cm^{-1}. The spectrum has resolved vibronic structure with the main progression consisting of a 1352 cm^{-1} spacing, similar to that in the $Me_2Au(acac)$ spectrum.

The emission spectrum of $Zn(hfac)_2{\cdot}2H_2O$ has an ligand-centered value of 22 500 cm^{-1} with a fwhm of 2200 cm^{-1}. This emission spectrum from this compound is the most resolved of those studied here. The two main progressions in the spectrum are created by a low-energy mode of 262 cm^{-1} and a high-energy mode of 1352 cm^{-1}.

Resonance Raman Spectrum of $Zn(hfac)_2{\cdot}2H_2O$. The resonance Raman spectrum of $Zn(hfac)_2{\cdot}2H_2O$ was measured using the 350.7 nm line from a Kr^+ ion laser. The peak at 1352 cm^{-1} is the most intense band in the spectrum. Other bands having intensities of greater than 5% of that of the most intense band are listed in Table 1. The Raman peaks are superimposed on a broad background emission making the measurement of the Raman intensities more difficult. The intensities, with an experimental uncertainty estimated at ±20%, are listed in Table 1.

Discussion

1. Assignment of the Emission Spectra. The low temperature emission spectra of the β-diketonate complexes give direct support for the ligand-centered π^* to π assignment of the emission band. The most important general supporting feature is that, for a given ligand, the energy of the emission is not very sensitive to the metal. In the case of the hfac complexes, no change in E_{00} is observed when the metal is changed from gold to zinc. In the case of the acac complexes, changing the metal from gold to aluminum only changes the value of E_{00} by 700 cm^{-1}. The onset of the emission bands moves only slightly in energy with changes in the fluorine content in the acetylacetonate ligand. The acac compounds emit at a slightly higher energy than the tfac compound, and the tfac compound emits at slightly higher energy than the hfac compounds. These small shifts are caused by the perturbations on the π orbital energies by the substituent CF_3 groups. A similar trend was reported for the energies of the spin allowed $\pi-\pi^*$ absorption bands of iron(III) complexes.[9] The spin-forbidden absorption bands occur below 23 000−24 000 cm^{-1} and have molar absorptivities of <1 M^{-1} cm^{-1}.[1,9]

The second important spectroscopic result that supports the ligand-centered π^* to π assignment is the observation that the only active modes in the series of emission spectra are ligand-centered modes. The main ligand mode that is observed is the 1352 cm^{-1} vibration; in addition the 262 cm^{-1} mode is sometimes resolved. This result, discussed below in more detail in connection with the emission spectrum of the zinc compound, indicates that the major bond length and bond angle changes caused by the transition occur between atoms on the ligand, as expected for a π^* to π ligand-centered transition.

The resonance Raman results are also in agreement with the π^* to π assignment. The vibrational normal modes that are most strongly resonance enhanced are those undergoing the largest distortions as a result of the electronic transition. All of the modes with intensities at least 5% of that of the most intense band are ligand-centered modes (Table 2).[16−19]

2. Calculation of the Distortions of $Zn(hfac)_2{\cdot}2H_2O$ from the Resonance Raman Spectrum. The relative bond distortions were calculated from the observed resonance Raman intensities and frequencies using Savin's formula[20−22]

$$\frac{\Delta_k}{\Delta_{k'}} = \left(\frac{I_k \omega_{k'}^{2}}{I_{k'} \omega_k^{2}}\right)^{1/2} \tag{4}$$

where Δ_k and $\Delta_{k'}$ are the dimensionless bond distortions, I_k and $I_{k'}$ are the resonance Raman intensities, and ω_k and $\omega_{k'}$ are the vibrational frequencies of the normal modes k and k'. The magnitudes of the individual distortions were calculated from

$$2\sigma^2 = \sum_k \Delta_k^{2} \omega_k^{2} \tag{5}$$

where $2\sigma^2$ is the full width of the absorption spectrum at half of its height. The bond distortions calculated (in dimensionless units)[23] using eqs 4 and 5 are given in Table 2. The calculated bond distortions provide a good estimate of the changes that occur as a result of the electronic transition. They are not exact values for two reasons. First, the experimental uncertainty is large because of the large emission background in the experimental spectra. Second, the Savin formula only takes into account one electronic state and neglects possible effects from nearby states.[24,25] Thus, the values calculated in Table 2 were

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Table 1. Input Parameters Used in the Time-Dependent Theoretical Calculations of the Emission Spectra of Metal-Acetylacetonate Compounds

compound	E_{00} (cm^{-1})	Δ(1352 cm^{-1})[a]	Δ(262 cm^{-1})[a]	Δ(1050 cm^{-1})[a]	Δ(748 cm^{-1})[a]	Γ (cm^{-1})
$Zn(hfac)_2 \cdot H_2O$	22 140	1.08	1.74	0.41	0.89	85
$Me_2Au(hfac)$[b]	22 140	1.52	1.44	0.87	N/A	74
$Me_2Au(tfac)$	23 100	1.74	1.37	N/A	N/A	305
$Me_2Au(acac)$	22 920	1.6	0.6	N/A	N/A	325
$Al(acac)_3$	22 220	1.6	0.6	N/A	N/A	550

[a] Distortions are given in unitless dimensions. [b] Data discussed in ref 6.

Table 2. Resonance Raman Intensities and Calculated Distortions for $Zn(hfacac)_2 \cdot H_2O$

frequency of normal mode (cm^{-1})	assign[a]	Savin formula distortion (Δ)	Raman intensity (I_k)	distortion used in calcn (Δ)
1660	C=C str	0.29	0.056	0.29
1545	C−O str + CH bend	0.35	0.067	0.35
1352	C-C str + C-CF_3 str	1.53	1.0	1.08
1050	C−CF_3 rock	1.18	0.392	0.41
748	C−CF_3 str	0.50	0.033	0.89
262	ring def	1.80	0.052	1.74

a Reference 19.

used as the starting point for the theoretical fit to the $Zn(hfac)_2 \cdot 2H_2O$ emission spectrum.

3. Calculation of the Distortions of $Zn(hfac) \cdot 2(H_2O)$ from the Emission Spectrum. The experimental emission spectrum of $Zn(hfac) \cdot 2(H_2O)$ is the best resolved of the β-diketonate complexes that are studied in this paper. Progressions in the 1352 and 262 cm^{-1} modes are clearly observed. In order to analyze the spectrum as completely as possible, all of the modes that have significant distortions as determined from the resonance Raman analysis are used to calculate the emission spectrum. The best fit of the spectrum, calculated by using eqs 1−3 and the parameters from Table 2 is shown in Figure 1.

The calculated spectrum is in excellent agreement with the experimental spectrum. The distortions that give the best fit to the emission spectrum are within the experimental uncertainty of those determined from the resonance Raman spectrum. The reasons that the agreement is not exact are the experimental uncertainty caused by the large emission background in the experimental spectra and possible effects on the Raman intensities from nearby electronic states. Both the Raman-determined distortions and the emission-determined distortions show that the most highly distorted modes are ligand-centered modes, the C−C stretch and the O−C−C bend. In the one-electron picture, the transition resulting in the emission removes an electron from a π antibonding orbital on the ligand ring and places it in a π bonding orbital. This transition results in an increase in the π bonding. On the basis of this reasoning, the high frequency progression is interpreted to result from a decrease in the carbon-carbon bond length. [Note that the sign of the change cannot be obtained from the calculations because the distortions appear in eq 5 as the square.][23] The shortening of the C−C bonds will result in an increase in the O−C−C bond angles.

4. Calculation of the Emission Spectra of $Me_2Au(tfac)$, $Me_2Au(acac)$, and $Al(acac)_3$. The emission spectra of these three compounds are not as well resolved as that of the zinc compound. The spectra of both $Me_2Au(tfac)$ and $Me_2Au(acac)$-show a resolved progression in the 1352 cm^{-1} mode, whereas the spectrum of the aluminum compound consists of a featureless broad band. Because of the absence of detailed features, detailed fits of the emission spectra were not carried out. However, in order to be able to make rough comparisons to the zinc compound, rough fits using only the two modes that are the most highly displaced in the above analysis, the 1352 and the 262 cm^{-1} modes are carried out.

The parameters used in the rough fits shown in Figure 2 are given in Table 1. One feature of note is the fact that the distortions for the 1352 and the 262 cm^{-1} modes that give the best fits to the spectra of the two acac compounds, $Al(acac)_3$ and $Me_2Au(acac)$ are the same. The values of Γ differ due to the resolution in vibronic structure. The value of the distortion in the 1352 cm^{-1} mode in the best fit calculation of the emission spectrum of $Me_2Au(tfac)$ is very similar to that of the other two compounds, whereas the distortion in the 262 cm^{-1} mode is closer to that of the $Zn(hfac)_2 \cdot 2H_2O$ compound. The distortions given in Table 2 support the assignment of the emission bands as ligand-localized π^* to π transitions.

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(23) The formula to convert the dimensionless displacement Δ into Å is

$$\delta = \sqrt{\frac{6.023 \times 10^{23}}{M} \times \frac{h}{2\pi c\omega}} \times 10^{8}\Delta$$

where M is the mass involved in the vibration in the units of gram atomic weight (e.g. $C = 12$ g), ω is the wavenumber of the vibrational mode in cm−1, $\hbar = h/2\pi$ where h is Planck's constant in g cm2 s−1, c is the speed of light in cm s−1, δ is the displacement in Å, and Δ is the dimensionless displacement. For example, the bond length change for the 1352 cm−1 mode is 0.01 Å when the reduced mass is approximated as 6 g.

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