Photoionization of tris(2-phenylpyridine)iridium

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Abstract

An experimental study of the photoionization of gas phase tris(2-phenylpyridine)iridium, hereafter referred to as Ir(ppy)$_3$, is presented. One- and two-photon ionization studies yield a conservative estimate for the upper bound to the vertical ionization energy of 6.4 eV. The one-photon experiment was carried out using 193 nm radiation, and the latter experiments used tunable doubled dye laser radiation to excite the ligand-centered $^1$LC $\leftrightarrow$ $S_0$ transition, followed by photoionization. An accompanying paper presents a theoretical study of Ir(ppy)$_3$ excited singlets and triplets and low energy states of Ir(ppy)$_3^+$. The calculated ionization energy is $\sim$ 5.9 eV. Taking the experimental and calculated results together, including a calculation by Hay (5.94 eV), it is concluded that the ionization energy is in the vicinity of 6 eV. This is favorable from the perspective of organometallic light-emitting diode applications. An undulation in the ion yield spectrum ($\sim$ 270 cm$^{-1}$ spacing) was observed that is due possibly to structure in either the $^1$LC $\leftrightarrow$ $S_0$ transition or the ionization transition that originates from the $T_1$ state populated through radiationless decay of $^1$LC. It is interesting that the parent cation Ir(ppy)$_3^+$ is produced with no discernible fragmentation, despite the fact that a large amount of vibrational energy is present in the $T_1$ state that undergoes photoionization. Specifically, this vibrational energy is the sum of the energy difference between the photon and $T_1$ energies (i.e., $h\nu - E_{T_1}$) and the thermal energy of the 177 Ir(ppy)$_3$ vibrational degrees of freedom at 500 K, i.e., the temperature at which the experiments were carried out. As photoionization is mainly vertical, vibrational energy is transported efficiently to the cation.

**Keywords:** photoionization, ionization energy, internal conversion, intersystem crossing, radiationless decay, phosphorescence, iridium complexes, spin-orbit coupling, OLED.
1. Introduction

Electroluminescent diodes that use organic and organometallic materials are referred to as organic (organometallic) light emitting diodes (OLED's). Such devices and the materials that comprise them have been the subject of intense research in recent years due to numerous potential (and to a large extent inevitable) applications, most notably in display technologies [1-5]. The optimization of a given device architecture requires attention to the many interactions that transpire within and among the constituents. In this paper the photoionization of one of the most important OLED species: tris(2-phenylpyridine)iridium, hereafter referred to as Ir(ppy)$_3$, is examined. A few introductory comments are given below to provide context for what follows. The recent book by Yersin [1] and the review article by Yersin and Finkenzeller [2] provide excellent overviews of the state-of-the-art of OLED research, including a number of fundamental electronic structure considerations.

Figure 1. This schematic indicates important features of an OLED (not to scale, typical dimensions are given in parentheses). Electrons are injected from the cathode through a thin protection layer into the electron transport layer, which typically consists of an amorphous organic material. Holes are injected into the hole transport layer from an optically transparent anode (typically an In$_2$O$_3$/SnO$_2$ composite) that permits light to exit the device. In the recombination and emission layer, electron-hole pairs form excitons that relax to the dopant excited states (indicated by an asterisk *) that emit photons. Adapted from [2].

A typical device consists of layers of compounds sandwiched between electrodes that inject electrons and holes into layers [1-5]. Figure 1 illustrates the most important features. A number of additional layers that further enhance device performance have been omitted to facilitate...
focusing on the most important processes. When a voltage is applied across the electrodes, electrons are injected from the cathode through a thin (typically ≤ 1 nm) electron injection and protection layer into the lowest unoccupied molecular orbitals (LUMO's) of molecules in the electron transport layer, which typically consists of an amorphous material such as Alq3 (q = 8quinolinolato-O,N) [6,7]. The injected electrons migrate slowly by directed site-to-site (polaron) hopping driven by the applied field.

The anode injects holes by removing electrons from the highest occupied molecular orbitals (HOMO's) of molecules in the hole-transport layer. The electrons and holes move toward each other under the influence of the field and form excitons in an emitter-doped recombination layer. Ideally, the excitons are highly excited states of the emitter molecules, rather than of the organic host, though the latter also can also result (ultimately) in the desired excitation [8]. Electronic excitation cascades down to the molecular excited states (indicated by an asterisk *) that emit photons. The photons exit via the optically transparent anode, which typically consists of a mixture of In2O3 and SnO2, i.e., indium tin oxide (ITO) [4,5].

Each charge carrier has spin. In the case of a hole, the spin is that of the residual electron. Because the spins of a combining electron and hole are uncorrelated, both singlet and triplet excitons are formed. Specifically, the spins combine to give one singlet and three triplets. It is generally accepted that each of the four states is formed with equal probability. In other words, three triplets are created for each singlet [1-3,9].

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Figure 2. (a) Organic molecules (negligible spin-orbit coupling) emit only from the lowest excited singlet $S_1$. Because $T_1 → S_0$ emission is extremely weak, triplet excitation is lost through radiationless decay rather than photon emission, and consequently the maximum quantum yield is 25%. (b) In triplet harvesting, electron-hole recombination leads to excitons having a triplet-to-singlet population ratio of 3:1. Excitation cascades down the triplet and singlet manifolds, with internal conversion (IC) and intersystem crossing (ISC) resulting in excitation ultimately residing in the lowest triplet, $^3$MLCT ($T_1$), which emits photons. An organometallic compound (in which spin-orbit coupling (SOC) is strong) such as Ir(ppy)$_3$ experiences relatively fast ISC and efficient $T_1 → S_0$ phosphorescence. This can result in quantum yield approaching 100%.
Referring to Fig. 2(a), following the cascade from the initially formed excitons to lower energies, organic emitters, e.g., polyfluorenes [10], undergo fluorescence from the excited singlet $S_1$. Phosphorescence from the lowest triplet (whose sublevels are shown separated from one another for clarity) is, for all practical purposes, eliminated because of the long triplet spontaneous emission lifetimes that are characteristic of the weak spin-orbit coupling (SOC) regime. Because of these long spontaneous emission lifetimes, $T_1$ decays non-radiatively. As a result, organic emitters have low electroluminescent quantum yield [11]. In the limit of negligible $T_1 \to S_0$ emission, the maximum quantum yield is 25%.

Certain metal-ligand complexes undergo efficient phosphorescence following photoexcitation and/or the passage of electric current through solid hosts that contain these complexes [4-7,12]. As mentioned earlier, the latter means of excitation is attractive from the point of view of display technologies. Among the most promising of these complexes is Ir(ppy)$_3$ and similar species [3]. Seminal and extensive contributions by the groups of Thompson [4,12,14,15], Forrest [4,12,13,15], and Yersin [16,17] have demonstrated the high potential of this system, and promising paths to device fabrication have been identified [2,4-7,12,15]. Related materials can be used to obtain different emission wavelengths such that the primary colors (red, green, and blue) are obtained. For example, this tuning can be achieved by using electron withdrawing and donating groups substituted at the ppy (2-phenylpyridine) ligand [15,18].

Referring to Fig. 2(b), the triplet states can be made to do useful work by employing a transition metal complex in which the transition-metal atom is responsible for strong SOC [1-3]. In such cases, the intersystem crossing (ISC) rate from $^1$MLCT to $^3$MLCT ($T_1$) is sufficiently fast to inhibit fluorescence from the lowest excited singlet [19-22]. The acronym MLCT stands for metal-to-ligand charge transfer. This label can be somewhat misleading, as the situation can be more complicated [23-25]. For the sake of brevity, hereafter we shall use the label $T_1$ instead of $^3$MLCT, with the understanding that this $T_1$ bears no resemblance to the one in Fig. 2(a), in the sense that it contains enough singlet character to ensure high phosphorescence quantum yields. As a result of efficient energy transfer processes, both singlet and triplet excitons populate the $T_1$ substates, which decay predominantly via phosphorescence.

This is referred to as triplet harvesting [1-3]. Strong SOC significantly increases the phosphorescence rate, enabling it to compete favorably with radiationless decay, and quantum yields therefore can approach 100% [6,12]. A number of organometallic (specifically, organo-transition-metal) complexes have been used as phosphor dopants in OLED's to overcome the efficiency limit imposed by the absence of sufficient spin-orbit interaction [1-3,26].

Internal conversion (IC) and ISC mechanisms are enlisted frequently. Though understood separately, these are unruly in systems that consist of many potential energy surfaces (PES's), unknown coupling parameters, and condensed phase host environments, leaving open important issues: (i) electronic structure of low-lying singlets and triplets including the role of spin-orbit interaction; (ii) vibrational relaxation, e.g., from the regime of quantum chaos to that of good quantum numbers; (iii) interactions with host environments; (iv) electron-hole recombination and transport; and so on.
Figure 3. (a) Photoexcitation of ligand-centered $^{1}\text{LC}(\pi\pi^*)$ is accompanied by rapid radiationless decay: IC to $^{1}\text{MLCT}$ followed by ISC to the levels labeled $T_1$ (energies are not to scale) [28]. (b) Absorption spectrum of Ir(ppy)$_3$ in dimethylformamide at 414 K. Note the large $\sigma_1$ absorption cross-sections ($i.e.$, units of $10^{-16}$ cm$^2$) [29]. The boxed region, 34 150 – 35 775 cm$^{-1}$ (4.234 – 4.435 eV), corresponds to the portion of the $^{1}\text{LC} \leftarrow S_0$ system examined in this work. Inset: changing the temperature over the range 295 – 414 K has a minimal effect on the absorption spectrum in the energy range of interest; only slight broadening is observed. In order, from the top trace, the temperatures are: 295, 333, 353, 383, 408, and 414 K. The vertical axis in the inset is not labeled, as the curves are offset from one another for clarity. They are nearly identical over the indicated range. (c) Absorption spectrum of 2-phenylpyridine, adapted from [30]. The $^{1}\text{LC} \leftarrow S_0$ feature is analogous to the one in Ir(ppy)$_3$. 

\[ \text{Ir(ppy)}_3^+ + e^- \rightarrow ^1\text{MLCT} \rightarrow ^1\text{LC}(\pi\pi^*) \rightarrow ^1\text{MLCT} \rightarrow T_1 \]

\[ \text{S}_0 \rightarrow ^1\text{MLCT} \rightarrow ^1\text{LC}(\pi\pi^*) \rightarrow ^1\text{MLCT} \rightarrow T_1 \]
Not surprisingly, many singlets and triplets in the energy region of interest need to be taken into consideration. SOC is effective because of near resonances among singlets and triplets, as well as approximate symmetries. Crossings and near crossings of PES's facilitate couplings, and this likely plays an important role. For Ir(ppy)$_3$, the papers of Nozaki and Nozaki and coworkers do a good job of combining SOC with time dependent density functional theory (TDDFT) calculations of low-lying singlets and triplets [25,27]. For example, Table 6 in reference [25] lists energy, singlet fraction, and oscillator strength for 140 low-lying excited states. It is seen that spin-orbit interaction plays an important role in coupling the triplet and singlet manifolds.

To understand what happens in OLED devices, our understanding of an isolated entity such as Ir(ppy)$_3$ must evolve to one of the larger system of Ir(ppy)$_3$ plus its host. In principle we would like to refine the theory of an isolated molecule such as Ir(ppy)$_3$ as much as possible before addressing the challenge presented by the environment. To this end, one of the most important and fundamental properties of a molecule is its ionization: vertical and adiabatic ionization energies, associated orbital and structural changes, etc. Yet, little is known about the ionization of Ir(ppy)$_3$. This is one of the factors that motivated the present study, in which the photoionization of gaseous Ir(ppy)$_3$ has been examined using a 2-photon photoionization scheme in which the ligand-centered 1LC($\pi\pi^*$) state, hereafter referred to as 1LC, serves as the intermediate (Fig. 3). The 1LC state is, however, an interesting intermediate in that radiationless processes (IC and ISC) rapidly transfer excitation to T$_1$, from which photoionization takes place. A 1-photon photoionization experiment (i.e., using 193.3 nm radiation from an ArF excimer laser) was carried out as well.

Referring to Fig. 3, it proved possible to isolate 2-photon photoionization and characterize it over the portion of the 1LC $\rightarrow$ S$_0$ system indicated by the yellow box. It turned out that photoionization could be achieved with no discernible ion fragmentation. In other words, at sufficiently low fluence, the parent ion, Ir(ppy)$_3^+$, dominates the mass spectrum. Large molecules such as Ir(ppy)$_3$ have a high density of electronic states at energies near and above ionization threshold, and it is not always feasible to eliminate the absorption of photons beyond the ionizing transition. In the present case, however, the very large $\sigma_1$ values (i.e., $>10^{-16}$ cm$^2$ [29], see Fig. 3) and, following absorption of the second photon, rapid radiationless decay in competition with ionization (discussed later) help make this possible.

From these 2-photon photoionization experiments, an upper bound to the vertical ionization energy (VIE) was obtained subject to a reasonable assumption about the disposition of Ir(ppy)$_3$ vibrational energy in the Ir(ppy)$_3^+$ ion, namely, that T$_1$ vibrational excitation is transferred more-or-less intact to the cation [31]. As mentioned above, 1-photon photoionization at 193.3 nm (51730 cm$^{-1}$, 6.414 eV) was also achieved. Again using the assumption that parent vibrational excitation is carried over to the cation yields an approximate upper bound of 6.4 eV. This value agrees with calculations carried out in our group, which places both the VIE and the adiabatic ionization energy (AIE) at approximately 5.9 eV, as well as a previous calculation that places the VIE at approximately 5.94 eV [32].

It is concluded that the ionization energy (both VIE and AIE) of gaseous Ir(ppy)$_3$ is in the vicinity of 6 eV. This is at odds with a value of 7.2 eV surmised from energy loss spectra, indicating the need to reinterpret the peak at 7.2 eV in the energy loss spectra [33]. It is also shown
that the absorption spectrum can be reproduced rather well using vertical excitation from the $S_0$ equilibrium geometry. This supports the assumption that vibrational excitation is carried more-or-less intact to the cation.

In the context of applications that involve organic photovoltaics (OPV's) and OLED's [1], a molecule's ionization energy (IE) is one of its key properties, as it quantifies a system's electron-donating ability and it is related to the reduction potential. For optimal performance of materials used in OLED devices, the IE's and electron affinities (EA's) (commonly referred to as HOMO and LUMO energies, respectively) of molecules in the active ($i.e.$, light-generating in OLED's and exciton-generating in OPV's) layer needs to be matched to the energy levels of the electrodes. The fact that the IE of Ir(ppy)$_3$ is low augurs well for its use in OLED devices. Indeed, it is significantly lower than those of either 2-phenylpyridine (8.0 eV) [34] or a bare iridium atom (8.967 eV) [35].
2. Experimental methods and results

The absorption spectra of Ir(ppy)$_3$ shown in Fig. 3 were recorded using a Varian Cary 300 spectrophotometer. Solutions were prepared by dissolving 6 mg of Ir(ppy)$_3$ (provided by the Thompson group at USC) in 125 mL of dimethylformamide (DMF). This solvent was chosen because its high boiling point (426 K) [36] enabled spectra to be collected at temperatures up to 414 K. Spectra were also recorded using the solvent dichloromethane (DCM). Though its UV transmission is superior to that of DMF, it cannot be used at the higher temperatures because its boiling point is 313 K [36]. No significant spectral differences were observed with these solvents. Heating was achieved by wrapping the cuvettes in resistive wire and passing current through the wire. Temperature was monitored with a thermocouple.

Figure 4. Schematic of the experimental arrangement: (a) The main vacuum chamber has a base pressure of $2 \times 10^{-9}$ Torr. (b) Details of the time-of-flight mass spectrometer (TOFMS): Typical mass resolution was $m/\Delta m \sim 200$. Laser photoionization was carried out in a chamber that was evacuated using a turbomolecular pump (Leybold Turbvac 1000C), as indicated in Fig. 4(a). The base pressure was $2 \times 10^{-9}$ Torr. Solid Ir(ppy)$_3$ was loaded into a stainless steel cylinder and a 0.5 cm diameter aperture allowed Ir(ppy)$_3$ vapor to effuse into the chamber. The cylinder was heated using resistive wire. During operation, the cylinder temperature was maintained at approximately 500 K, and the
chamber pressure was $5 \times 10^{-9}$ Torr. At 500 K there was no thermal decomposition of the Ir(ppy)$_3^+$ sample.

Referring to Fig. 4, mass spectra were recorded using a time-of-flight mass spectrometer (TOFMS). Photoions were produced between two electrodes: a repeller plate and an extractor that consists of a metal ring with a fine nickel mesh in the center. Ions receive an additional 2 kV of kinetic energy after passing through the extractor. They then drift for 51.3 cm before arriving at the double-chevron microchannel plate (MCP) detector. The two meshes indicated with red provide a ground shield, ensuring a field-free drift region. Calibration was carried out using NO photoionization with a variety of voltages applied to the electrodes. The NO$^+$ flight times, in combination with the distances indicated in Fig. 4 (i.e., $d = 0.7$ cm, $s = 0.62$ cm, and $\delta s \sim 0.7$ mm), enabled the length of the drift region to be determined accurately.

Resolution was optimized at the parent ion mass by adjusting the experimental parameters to make the Ir(ppy)$_3^+$ peak as narrow as possible. Voltages of 2.36 and 2.00 kV were applied to the repeller and extractor electrodes, respectively. A voltage of approximately $-1.9$ kV was applied to the MCP detector. The magnitude of this voltage was increased over time to counteract de-
gradation of the detector. Signal acquisition was carried out using a dual channel Gage Com- puscope CS-8012A. The sample rate was 100 MS/s, providing 10 ns bin widths. The repetition rates were those of the lasers, 20 Hz for the 2-photon studies and 10 Hz for the 1-photon study. Typically, ~ 1000 individual spectra were summed. The TOF spectra were processed using custom Labview 8.5.1 programs to yield the mass spectra.

Under these conditions, the Ir(ppy)$_3$$^+$ signal shown in Fig. 5(a) (solid black line) was recorded using 35 673 cm$^{-1}$ (4.423 eV) radiation and a fluence of 415 µJ cm$^{-2}$. The trace shown is the average of several traces. The peak has a full width at half maximum (FWHM) of approximately 3.6 amu. A significant percentage of this width is due to the isotopic composition of the Ir(ppy)$_3$ sample. Though the natural abundance of $^{13}$C is only 1.07%, Ir(ppy)$_3$$^+$ contains 33 carbon atoms. Consequently, (rounded to the nearest tenth of a percent) 70.1% of the Ir(ppy)$_3$ molecules contain only $^{12}$C atoms, 25.0% contain one $^{13}$C atom, 4.3% contain two $^{13}$C atoms, 0.5% contain three $^{13}$C atoms, and a negligible percentage contain more than three $^{13}$C atoms. Thus, $^{13}$C plays a significant role in the mass spectra. Including the natural abundances of the two iridium isotopes (i.e., 62.7% and 37.3% for 193 and 191 amu, respectively) yields the following isotopologues, where the subscript on C denotes the number of $^{13}$C atoms in Ir(ppy)$_3$:

$^{191}$Ir/$^{13}$C$_0$ 653 amu 26.2%  
$^{191}$Ir/$^{13}$C$_1$ 654 amu 9.3%  
$^{191}$Ir/$^{13}$C$_2$ 655 amu 1.6%  
$^{191}$Ir/$^{13}$C$_3$ 656 amu 0.2%  

$^{193}$Ir/$^{13}$C$_0$ 655 amu 44.0%  
$^{193}$Ir/$^{13}$C$_1$ 656 amu 15.7%  
$^{193}$Ir/$^{13}$C$_2$ 657 amu 2.7%  
$^{193}$Ir/$^{13}$C$_3$ 658 amu 0.3%

The percentages of the relevant masses are: 653 (26.2%); 654 (9.3%); 655 (45.6%); 656 (15.9%); 657 (2.7%); and 658 (0.3%). All but the last of these (which is negligible for the purpose of fitting the curve) are represented by the Gaussian curves indicated in Fig. 5(b) that were used to fit the peak in Fig. 5(a). In other words, the peak heights of the contributions in Fig. 5(b) are proportional to their respective abundances. Each of the constituent peaks was assigned a FWHM of 2.35 amu. This choice is ad hoc. If one wishes, it can be interpreted as a rough measure of the instrumental resolution at 655 amu. Summing the curves in (b) yields the blue curve in (a), which fits the experimental data (red curve).
2.1. Multiphoton ionization

Photoionization was carried out using a tunable dye laser and a variety of dye mixtures to cover a reasonable portion of the $^1\text{LC} \leftarrow \text{S}_0$ system. The dye laser (Continuum HD 6000) was pumped with the second harmonic of a 10 ns, 20 Hz Nd:YAG laser (Continuum Powerlite 9020). Mixtures of rhodamine 590 and 610 (Exciton) were used. The use of these dye mixtures enabled different tuning ranges to be achieved with the kind of stable, long-term operation that is needed to obtain quantitative 2-photon spectra. The dye laser output was doubled using a KDP crystal in a UV frequency extender (Continuum UVT-3), yielding radiation in the region 279–292 nm.

The laser radiation was focused using a 60 cm lens to a diameter of approximately 0.7 mm, resulting in a maximum fluence of approximately 1500 mJ cm$^{-2}$. The TOF spectrum obtained using this fluence and a photon energy of 35 774 cm$^{-1}$ (4.435 eV) is shown in Fig. 6. The most intense peak (i.e., the doublet centered at 192 amu) is split according to the natural isotopes of iridium. The less intense doublet centered at 204 amu is due to $^{191}\text{IrC}^+$ and $^{193}\text{IrC}^+$. Signals due to Ir(ppy)$_2^+$ and Ir(ppy)$_3^+$ (not shown) are an order of magnitude smaller than the Ir$^+$ peak. The cluster of peaks at lower mass is unaffected by source temperature and it is present in the absence of Ir(ppy)$_3$. Therefore, these peaks are attributed to hydrocarbon contamination.

Figure 6. At a fluence of 1500 mJ cm$^{-2}$ and photon energy of 35 774 cm$^{-1}$ (4.435 eV), the mass spectrum is dominated by Ir$^+$, albeit with an IrC$^+$ contribution that is ~15% as large as that of Ir$^+$. Contributions from Ir(ppy)$_2^+$ and Ir(ppy)$_3^+$ (not shown) are smaller by an order of magnitude. The hydrocarbon peaks are due to impurity.

Figure 7(a) shows the intensity of the Ir$^+$ signal as a function of photon energy in the range 34 900–35 800 cm$^{-1}$ (4.327 – 4.438 eV) Fluence of approximately 1400 mJ cm$^{-2}$ was used. The spectrum consists of a number of sharp peaks superimposed on a weak continuum. The only significant effect observed upon increasing the fluence is to increase the amount of underlying continuum. The boxed area is expanded in Fig. 7(b). The vertical dashed lines correspond to transitions of neutral atomic iridium. The agreement between the measured spectrum and the dashed lines indicates that the sharp features are due to multiphoton ionization of atomic iridium [37], itself arising from multiple photon processes. In such high fluence cases, amusing spectra can be recorded, but obtaining detailed information about the low-lying excited states of Ir(ppy)$_3$ is not feasible [38].
At the same time, an important fact follows from atomic iridium spectra such as those shown in Fig. 7. They indicate that, at least under high fluence conditions, photofragmentation is so severe as to yield significant quantities of iridium atoms that then undergo multiphoton ionization. In fact, neutral photofragmentation dominates. Were neutral iridium atoms produced via photo-
dissociation of an ion precursor, there would have to be an ion partner. There is no evidence whatsoever of Ir(ppy)$^+$, and only a small ppy$^+$ signal appears at high fluence. The dominance of neutral fragmentation channels is not surprising, given that previous studies have shown that photolysis is a common, often dominant, pathway for photoexcited organometallic compounds [39-45]. The important conclusion is that the ionization and neutral fragmentation channels are in competition with one another. This bears on interpretation of the ion yield spectra (vide infra Fig. 10), as discussed later.

2.2. Two-photon ionization

An attenuator consisting of a half-wave plate and a Glan-Thompson polarizer was inserted into the beam path. This allowed the laser fluence to be varied over a broad range with good accuracy, with the caveat that this fluence is an average over the near-Gaussian beam shape. First, the polarizer is set for maximum transmission. Then the half-wave plate is inserted between the light source and the polarizer. Fluence is easily adjusted by turning the half-wave plate. Because focusing limits the lowest fluence that can be obtained using this procedure, the focusing lens was removed to examine the low fluence regime. In this case, the radiation passed through a 1 mm diameter aperture. This enabled fluence as low as 50 $\mu$J cm$^{-2}$ to be achieved with good accuracy. Diffraction over the aperture-sample distance was minimal.

Figure 8. Mass spectra recorded at different fluences: The laser frequency is 35357 cm$^{-1}$ (4.383 eV) At low fluence (bottom trace), photoionization produces the Ir(ppy)$^+_3$ ion exclusively. As the fluence is increased, fragmentation results in the appearance of the Ir(ppy)$^+_2$ ion. At high fluence (top trace), the Ir$^+$ peak dominates, indicating severe fragmentation of Ir(ppy)$^+_3$ and its photofragments.
Figure 8 shows how changing the fluence affects the mass spectra. The highest fluence (top trace) yields a mass spectrum that is similar to the one presented in Fig. 6. The Ir\(^+\) peak dominates. Signals corresponding to Ir(ppy)\(_2\)\(^+\) and Ir(ppy)\(_3\)\(^+\) gain intensity as the fluence is decreased. At 88 mJ cm\(^{-2}\), the Ir\(^+\) and Ir(ppy)\(_3\)\(^+\) peaks have approximately equal height, and an IrC\(_n\)\(^+\)/IrN\(_n\)\(^+\) progression has emerged. When the fluence is below \(\sim 1.6\) mJ cm\(^{-2}\), the Ir(ppy)\(_3\)\(^+\) parent ion is isolated, i.e., the mass spectrum, for all practical purposes, contains no other peaks. No signal corresponding to Ir(ppy)\(^+\) has been observed in any of the experiments.

Generally, the parent ion is most useful for acquiring information about the molecule and therefore this signal was the main focus of the present study. It should be noted that it was not obvious \textit{a priori} that it would be possible to isolate the parent ion, particularly in light of the large amount of parent vibrational energy that is present at 500 K. Thus, it was pleasing to find that Ir(ppy)\(_3\)\(^+\) was the only ion peak in the mass spectrum over a wide range of experimental conditions.

The fluence dependence of the Ir(ppy)\(_3\)\(^+\) signal revealed that it is proportional to the second power of the laser fluence, as long as the fluence is less than \(\sim 1.6\) mJ cm\(^{-2}\) (see Fig. 8). To be on the safe side, we shall take the low-fluence regime to be less than 1 mJ cm\(^{-2}\). Figure 9 shows a log-log plot of the Ir(ppy)\(_3\)\(^+\) signal versus fluence, \(\Phi\), obtained with a photon energy of 35420 cm\(^{-1}\) (4.391 eV). Similar results were obtained using a number of photon energies in the range 34207 – 35930 cm\(^{-1}\) (4.241 – 4.455 eV). At slightly higher fluence, but below the regime where significant fragmentation occurs, the Ir(ppy)\(_3\)\(^+\) signal is no longer proportional to \(\Phi^n\) with \(n = 2\). For example, the range 2-15 mJ cm\(^{-2}\) is characterized by \(n = 1.5\). This is consistent with some degree of saturation of one or both transitions, as well as a contribution from parent ion fragmentation.

The term saturation is most often used to describe the near equality of two state populations that is brought about through the application of an intense, resonant electromagnetic field. In the system under consideration here, the electronically excited states are unstable because of radiationless decay. Therefore, the term saturation is used advisedly, \textit{i.e.}, to describe the regime where the figure-of-merit \(\sigma\Phi\) assumes values of a few tenths or larger [46].
Figure 10. (a) Ir(ppy)$_3^+$ signal divided by fluence squared versus photon energy. The smooth curve at the top is the Ir(ppy)$_3$ absorption cross-section $\sigma_1$ (right vertical scale) in DMF at 414 K (from Fig. 3). Different ratios of rhodamine 590 and 610 and the corresponding energy regions are designated by horizontal double-sided arrows: (a) 100% 590 (279.5 – 283.1 nm); (b) 590:610 = 9:1 (281.5 – 284.3 nm); (c) 590:610 = 4:1 (283.2 – 286.8 nm); (d) 590:610 = 7:3 (286.2 – 288.1 nm); (e) 590:610 = 3:2 (287.8 – 290.5 nm); (f) 100% 610 (290.2 – 292.8 nm). (b) The structured spectrum is the ion signal (scaled by $\Phi^{-2}$) in (a) divided by the condensed phase absorption spectrum shown in (a). If the absorption spectra of gaseous and solvated Ir(ppy)$_3$ are the same, the structure in the yield spectrum is due to $\sigma_2$. Alternatively, if the structure is due to $\sigma_1$, the ionization cross-section can have smooth energy dependence, e.g., as indicated with the dashed blue curve in (b). The top scale in (b) indicates (roughly) the spacing of the undulation.
Figure 10(a) shows the "fluence-corrected" Ir(ppy)$_3^+$ signal versus photon energy in the range 34150–35775 cm$^{-1}$ (4.234–4.435 eV). Because the Ir(ppy)$_3^+$ signal varies as the second power of the laser fluence ($\Phi^2$) in these experiments, care was taken to ensure that the fluence did not deviate more than 5% from 450 µJ cm$^{-2}$. To this end, the spectrum in Fig. 10(a) is composed of six separate spectra recorded using different rhodamine 590 and 610 dye mixtures. The photon energy regions covered by the different dye mixtures are indicated using horizontal double-sided arrows. In addition, the laser fluence was recorded along with the ion signal, enabling the ion signal to be corrected for the modest change of fluence using the $\Phi^2$ dependence. This is the above-mentioned "fluence corrected" signal.

The trace in (b) is the trace in (a) divided by the absorption spectrum shown in Fig. 3. This latter spectrum is reproduced in Fig. 10(a) as the smooth curve at the top, whose scale is on the right hand side. If the gas phase spectrum has the same shape as the 414 K spectrum (DMF solvent) in Fig. 3, the trace in (b) represents the dependence of the ion signal on the ionizing photon energy. This is discussed in Section 3. The upper horizontal scale in (b) indicates that the undulation has spacing of roughly 270 cm$^{-1}$ (33 meV).

The undulation seen in Fig. 10(b) was unanticipated. If anything, a smooth variation of $\sigma_2$ versus photon energy was expected [47,48]. Therefore, the photoionization spectrum shown in Fig. 10 was examined thoroughly to ensure that it is not an artifact. The data were recorded with great care over several months, using six different dye solutions, ensuring that the laser fluence is safely within the 2-photon regime, and taking care to not mistake a variation of laser fluence for a variation of $\sigma_2$. There was no relationship between the undulation and the tuning ranges used with the various dye mixtures. The undulation was repeatable. Possible explanations are discussed in Section 3.

2.3. One-photon ionization

It also proved straightforward to photoionize Ir(ppy)$_3$ using a single 193.3 nm (6.414 eV) photon. The output from an ArF excimer laser (Lambda Physik Compex 201) was passed through a 0.7 mm × 12.7 mm aperture. Less than 1 mJ cm$^{-2}$ ($< 10^{15}$ photons cm$^{-2}$) provided quite adequate signal. No significant changes to the experimental arrangement indicated in Fig. 4 were required, i.e., only optics and triggering. The sole ion present in the mass spectrum was Ir(ppy)$_3^+$. The photon energy provides an additional estimate of an upper bound for the ionization energy, subject to a reasonable assumption about the role played by parent vibrational energy in photoionization, as discussed in the next section.
3. Discussion

Referring to Fig. 10, single-frequency 2-photon ionization was carried out using photon energies throughout the range 34150 – 35775 cm\(^{-1}\) (4.234 – 4.435 eV). The 2-photon nature of Ir(ppy)\(_3^+\) production in this range was verified at a number of photon energies by recording data of similar quality to those shown in Fig. 9. With photon energies smaller than 34150 cm\(^{-1}\) (4.234 eV) it was not possible to obtain such high quality fluence dependence data because the absorption cross-section \(\sigma_1\) diminishes toward smaller photon energy and our ultraviolet radiation source (doubled dye laser) is less stable.

It is noteworthy that with the convenient (and significantly smaller) photon energy 28170 cm\(^{-1}\) (3.492 eV, corresponding to 355 nm) it was not possible to identify a regime where the Ir(ppy)\(_3^+\) signal varies as the square of the fluence. Even though the 355 nm radiation was more stable than the radiation used throughout the range indicated in Fig. 10.

As mentioned above, one of the problems is that the cross-section for absorption of the first photon (\(\sigma_1\)) diminishes on the low energy side of the \(^1\)LC \(\leftrightarrow\) \(S_0\) peak indicated in Fig. 3. Consequently, increasing the fluence to overcome smaller \(\sigma_1\) values raises the specter of beginning to saturate the \(\sigma_2\) transition. Of course, the major unknown with 355 nm radiation is the participation of 3-photon processes, as 28170 cm\(^{-1}\) (3.492 eV) is quite a bit smaller than 34150 cm\(^{-1}\) (4.234 eV). For example, might 355 nm photoionization be, at least in part, a 3-photon process with some degree of saturation (at times) of the \(\sigma_2\) and \(\sigma_3\) transitions?

In consideration of the above issues, to be on the safe side, all of the spectral scans were limited to the range shown in Fig. 10. Thus, 34150 cm\(^{-1}\) (4.234 eV) was used to estimate a very conservative upper bound for the ionization threshold obtained via single-frequency 2-photon ionization, as discussed below.

3.1. Low-lying electronically excited states

Insight into energy transfer and photophysical properties of low-lying electronically excited states of Ir(ppy)\(_3\) is provided by previous experimental studies. The ones most germane to the present study are reviewed here.

It is well known that Ir(ppy)\(_3\) exhibits intense (\(i.e.,\) high quantum yield) phosphorescence from \(T_1\) with an apparent radiative (spontaneous emission) lifetime of approximately 1.6 µs at room temperature [16,17,20,24,28]. This lifetime is phenomenological in the sense that the three \(T_1\) sublevels separately have quite different radiative lifetimes: 116, 6.4, and 0.2 µs, as indicated in Fig. 11 [17]. It is interesting that the term phosphorescence is used with a radiative lifetime as short as 0.2 µs. Specifically, 0.2 µs is comparable to the spontaneous emission life-
times of a large number of allowed singlet-singlet transitions in small molecules. Keep in mind, however, that so short a lifetime does not, by itself, imply dominant singlet character of the excited state. Specifically, a lifetime of 0.2 μs can arise through the introduction of even modest amounts of 1LC and/or 1MLCT character into T1 via SOC.

Because of the short 1LC → S0 and 1MLCT → S0 spontaneous emission lifetimes (recall the large absorption cross-sections indicated in Fig. 3), only a modest percentage of 1LC and/or 1MLCT character is needed to account for the 0.2 μs lifetime. For example, an estimate of ~6 ns was obtained for the 1MLCT → S0 radiative lifetime. This was achieved through application of a Strickler-Berg analysis [49,50] to several molecules having similar spectral properties in the region of interest [30,51-53], and then scaling these lifetimes to the absorption spectrum shown in Fig. 3 [29]. This confirmed that only a few percent of 1MLCT character mixed into the T1 state is needed to account for the short lifetime of 0.2 μs.

The radiative and energy transfer processes that transpire among the three T1 sublevels are subtle. For example, the different spontaneous emission rates participate in proportion to the respective sublevel populations, which in turn depend on both the temperature and the energy transfer rates among the sublevels. This has been examined assiduously by Yersin and coworkers [16,17], who have established, through numerous and sophisticated experiments and modeling, the various energy transfer and radiative properties [16,17]. Suffice it to say that, leaving aside for the moment a detailed assignment of the electronic character of all low-lying singlets and triplets, the radiative and energy transfer processes of the T1 sublevels are well understood compared to other Ir(ppy)3 photophysical and energy transfer processes.

It must be kept in mind that non-radiative relaxation processes such as 1LC → 1MLCT and 1MLCT → T1, which appear commonly in the literature, are highly

![Diagram](image_url)

Figure 11. Some important properties and processes of low-lying electronic states are indicated schematically (not to scale). Rapid radiationless decay processes (IC and ISC, with respective lifetimes γIC and γISC) ensure efficient T1 production [28]. Spontaneous emission lifetimes (τrad) for the T1 sublevels indicated on the far right differ considerably, despite the fact that these levels are close in energy, i.e., 116, 6.4, and 0.2 μs for 19693, 19712, and 19863 cm⁻¹, respectively, in CH2Cl2 solvent [17]. At room temperature, an observed phosphorescence lifetime of 1.6 μs reflects the complex interplay that exists between the T1 levels. The horizontal lines (above the electronic origins) whose spacing decreases with energy indicate (schematically) vibrational levels. Adapted from references [17] and [28].
simplified (in a sense phenomenological) models. For example, in reality there are several triplets whose energies lie below that of $^1\text{LC}$, as well as surface crossings. Details of the electronic structure are discussed at length in the accompanying (following) paper, hereafter referred to as Paper II [54].

With the above caveat in mind, at energies above the $T_1$ origin region (Fig. 11), femtosecond resolution transient absorption measurements of Tang et al. have revealed ultrafast dynamics among the $^1\text{LC}$, $^1\text{MLCT}$, and $T_1$ states [28]. Referring to Figs. 3 and 11, ultrafast (100 fs) photoexcitation at 400 nm was used to access $^1\text{MLCT}$. It was found that absorptions at 520 and 580 nm appeared with time constants of 100 fs and 70 fs, respectively. These 520 and 580 nm absorptions remained constant up to the maximum achievable delay (for the given experimental arrangement) of 1.5 ns. The long-lived absorbing state was assigned to phosphorescent $T_1$, implicating rapid ISC (i.e., $\tau_{\text{ISC}}$ values of 100 fs and 70 fs), as indicated in Fig. 11. This result is consistent with the essentially complete absence of $^1\text{MLCT} \rightarrow S_0$ fluorescence that has been noted [17,20], even at low temperatures [17].

Next, $^1\text{LC}$ was excited at 266 nm, and the transient absorptions at 520 and 580 nm, each originating from $T_1$, were fit using a bi-exponential function [28]. With the shorter time constants fixed at the $\tau_{\text{ISC}}$ values (100 fs and 70 fs, respectively), the other time constants were found to be 300 fs and 350 fs, respectively (Fig. 11). These longer time constants were assigned to IC from $^1\text{LC}$ to $^1\text{MLCT}$, i.e., $\tau_{\text{IC}}$ in Fig. 11. The bottom line is that this study demonstrated that photoexcited Ir(ppy)$_3$ relaxes via $^1\text{MLCT}$ to phosphorescent $T_1$ on a sub-picosecond timescale. Complementary experiments by Hedley et al. used ultrafast methods to probe directly the short-lived $^1\text{MLCT}$ spontaneous emission that follows photoexcitation at 400 nm with 100 fs pulses [20]. These challenging experiments confirmed the results of Tang et al. [28], and also revealed rapid vibrational energy transfer processes, including intramolecular vibrational redistribution. Again, as impressive as these measurements are, one must keep in mind that the electronic structure is more complex that the simplified scheme indicated in Fig. 11.

In the gas phase environments of the experiments reported herein, an Ir(ppy)$_3$ molecule's energy is conserved (until it emits a photon) following its absorption of a single ultraviolet photon. Therefore, intramolecular processes take place at close to fixed energies, i.e., the photon energy plus a given molecule's internal energy due to thermal equilibrium. This differs from the condensed phase environments that have been used in previous studies of laser-initiated dynamics in the Ir(ppy)$_3$ system. In these latter cases, intramolecular processes take place simultaneously with Ir(ppy)$_3$–host interactions. It is safe to assume that processes that take place on time scales of 70-100 fs are completely in the intramolecular regime, and processes that transpire on time scales of 300-350 fs are predominantly intramolecular. In the picosecond regime, however, it is hard to justify the assumption of solely intramolecular mechanisms, as dopant-host vibrational energy transfer processes can be competitive with intramolecular processes. When normal modes are accurate descriptors, dopant-host vibrational energy transfer will likely be slower than intramolecular processes. On the other hand, in the higher-energy regime of vibrational (vibronic) quantum chaos, dopant-host vibrational energy transfer can be rapid [55]. This regime can be accessed through IC and ISC processes.
Rapid ISC and the resulting efficient quenching of singlet-singlet fluorescence are consequences of strong (or at least efficient) SOC. Several theoretical studies have addressed this issue [23-25,27]. Of particular note are those of Nozaki [25] and Nozaki and coworkers [27], who examined effects due to SOC in Ir(ppy)$_3$ and analogous systems. The Nozaki results on Ir(ppy)$_3$ [25] are in qualitative accord with the experimental results [28].

As a result of significant singlet-triplet mixing, it has been suggested that an appropriate picture might be one in which photoexcitation produces the strongly spin-mixed phosphorescent states directly, in which case the term ISC has little meaning [25]. In other words, in a regime where ISC has little or no meaning, the lifetime $\tau_{ISC}$ would not be observed. Instead, photoexcitation would access states of mixed $^1$MLCT/$^3$T$_1$ character, and each of these states would emit in proportion to its percentage $^1$MLCT character. This scenario differs from the case in which a temporally short pulse excites the system, with the pulse's spectral width exceeding significantly the mean energy spacing between adjacent eigenstates. A coherent superposition of eigenstates is created whose short time character is that of the "bright state." In the Tang et al. experiments (400 nm), the bright state given by this coherent superposition is $^1$MLCT. This enabled $\tau_{ISC}$ to be determined.

Indeed, calculations indicate that the emitting states are of predominantly triplet character [23-25], with only modest percentages of singlet character. This is in agreement with the dilution of the very short singlet-singlet spontaneous emission rates mentioned earlier, in which $^3$T$_1$ acquires a small percentage of singlet character due to SOC. As a testament to the reliability of the calculations, the radiative lifetimes were reproduced, at least qualitatively, when SOC was taken into account [24]. In any event, on the basis of all of the above work [23-25], it follows that sub-picosecond ISC dynamics are not at all surprising.

3.2. Photoionization

Less is known about the ionization of Ir(ppy)$_3$. This is an important fundamental process that enters the world of OLED's through the electron-hole recombination (exciton formation) that initiates the cascade down the energy "ladder" that terminates at $^3$T$_1$. Yet, only one experimental value for gas phase Ir(ppy)$_3$ appears in the literature (7.2 eV) [33], and this is based on indirect evidence, as discussed later. Properties such as the adiabatic and vertical ionization energies (AIE and VIE's) are accessible through studies of gas phase Ir(ppy)$_3$. Ideally, one would like to prepare samples in which the Ir(ppy)$_3$ molecules have as little internal excitation as possible. However, to maintain a steady-state of gas phase Ir(ppy)$_3$ requires elevated temperature, and removing the large amount of vibrational energy present at such temperatures is a daunting prospect to say the least, e.g., forget about using nozzle expansion methods. Even if Ir(ppy)$_3$ were somehow cooled vibrationally, considerable vibrational energy would still be implanted through the IC and ISC processes that follow and/or accompany photoexcitation. Clearly, the role played by Ir(ppy)$_3$ vibrational excitation must be taken into account.

There are two sources of vibrational excitation in the present experiments. First, consider the vibrational energy of a gas phase Ir(ppy)$_3$ molecule at thermal equilibrium. To obtain sufficient Ir(ppy)$_3$ density in the region where photoionization takes place (Fig. 6) required maintaining...
the oven temperature at approximately 490 K. The effusing Ir(ppy)$_3$ molecules contain considerable vibrational energy (discussed below) as well as, on average, $3kT/2 = 510$ cm$^{-1}$ of rotational energy. As mentioned above, a second source of vibrational energy arises through the first photoexcitation step, say at 34150 cm$^{-1}$ (4.234 eV). The implanted $^1$LC excitation undergoes rapid IC to $^1$MLCT, which in turn decays rapidly via ISC to $T_1$, whose origin lies at approximately 19700 cm$^{-1}$ (2.442 eV) [17]. Fortunately for OLED applications, $T_1$ does not undergo ISC to $S_0$ on any relevant time scale.

The amount of vibrational energy imparted via $^1$LC $\leftrightarrow S_0$ photoexcitation is taken as the difference between the photon energy and the $T_1$ electronic energy, *i.e.*, $34150 - 19700 = 14450$ cm$^{-1}$ (1.791 eV). Of course, vestiges of $^1$LC and $^1$MLCT electronic excitations remain because gas phase Ir(ppy)$_3$ has no way other than photon emission to lower its energy. However, these contributions are minor because of the high density of $T_1$ vibrational states relative to the densities of vibrational states in the $^1$LC and $^1$MLCT manifolds at the 34150 cm$^{-1}$ (4.234 eV) photon energy.

It is now assumed that vibrational excitation plays a spectator role in photoionization, *i.e.*, all vibrational excitation in Ir(ppy)$_3$, regardless of how it got there or the specific form it might have, appears as vibrational excitation of the Ir(ppy)$_3^+$ cation. In other words, all Franck-Condon factors between $T_1$ and the cation are taken as diagonal, *i.e.*, $\langle m\nu_i|n\nu_k' \rangle = \delta_{mn}\delta_{ik}$, where $i$ and $k$ denote vibrational degrees of freedom such as normal modes, $m$ and $n$ denote numbers of quanta, and the prime denotes the ion. Note that the equilibrium geometry of the cation is quite close to that of $T_1$ (*vide infra* Table 1), which supports this assumption. Thus, the resulting very conservative upper bound to the ionization energy obtained through single-frequency 2-photon ionization is estimated to be the photon energy plus the $T_1$ electronic energy, *i.e.*, $34150 + 19700 = 53850$ cm$^{-1} = 6.67$ eV.

Let us now turn to 1-photon photoionization. As discussed in Section 2, it was possible to photoionize 490 K Ir(ppy)$_3$ vapor using 193.3 nm (6.414 eV) radiation. Again, if it is assumed that all vibrational excitation is transferred intact, this time from $S_0$ to the cation, a rough upper bound of 6.4 eV is obtained for the VIE. We shall take this to be the experimentally determined upper bound to the VIE, again subject to the assumption that parent vibrational energy is transferred more-or-less intact to the cation. Not surprisingly, it turns out that the AIE and VIE’s from $S_0$ and $T_1$ geometries do not differ much from one another, as discussed below.
3.3. Ion yield spectrum

The 2-photon Ir(ppy)$_3^+$ yield spectrum shown in Fig. 10 displays an undulation whose peak-to-peak spacing is \( \sim 270 \text{ cm}^{-1} (33 \text{ meV}) \). As mentioned earlier, these data were recorded over several months, using six different dye solutions, ensuring that the laser fluence is safely within the 2-photon regime, and taking care to not mistake a variation of laser fluence for structure in the ion yield spectrum. Possible origins of this undulation are now discussed.

Large IC rates, such as the one determined experimentally for $^1$LC $\rightarrow$ $^1$MLCT [28], are consistent with nonadiabatic transitions between potential surfaces taking place via one or more conical intersections. In large systems like Ir(ppy)$_3$, the search for such intersections presents a daunting computational challenge, so much so that it is not clear that the benefit merits the effort. Nonetheless, it is well known that this is a common and efficient mechanism for the IC of electronically excited states that can leave a fingerprint in the form of selective vibrational excitation in one or more modes. In general this could be manifest in the first and/or second photo-excitation steps, accounting for the observed structure, as discussed below.

One possibility is that the energy dependence of the cross section for absorption of the first photon, $\sigma_1(E)$, is responsible for the observed structure. There is no report in the literature of an ultraviolet absorption spectrum of either gaseous Ir(ppy)$_3$, or even of 2-phenylpyridine. Though spectra of these species in solvent display no hint of structure in the region of interest (Fig. 3), this does not imply that the corresponding spectra of gaseous samples are also smooth. Thus, the issue of possible structure in $\sigma_1(E)$ for gaseous Ir(ppy)$_3$ remains open. If, in fact, $\sigma_1(E)$ for gaseous Ir(ppy)$_3$ has structure that matches that of the ion yield spectrum, the cross section for the absorption of the second photon, $\sigma_2(E)$, may well have smooth variation. This is reasonable: $T_1$ and $D_0$ have very similar equilibrium geometries (vide infra Table 1), so there is no reason to expect photoionization alone to lead to a vibrational progression that is manifest in the ion yield spectrum. Such smooth variation of $\sigma_2(E)$ is indicated schematically by the blue dashed curve in Fig. 10(b).

Another possibility is competition between the ionization and radiationless decay pathways. In light of the fact that $^1$LC $\leftrightarrow S_0$ photoexcitation leads (via the $^1$MLCT intermediate) to $T_1$ on a sub-picosecond timescale, the absorption of the second photon can take place via one or more predominantly triplet-triplet transitions, with $T_1$ being the lower state. It is unlikely that the excited state thus produced fluoresces to any significant extent. Rather, it is expected to either ionize or undergo IC and/or ISC. As mentioned above, a signature of IC via conical intersection is selective vibrational excitation, and it is likely that efficient ISC behaves similarly. Even if the photoionization cross-section has no such structure, such a mechanism — radiationless decay in competition with ionization — can account for the spectrum in Fig. 10.

Given such possibilities, including combinations thereof and other scenarios, we are remiss to speculate further on the origin of the undulation indicated in Fig. 10.
3.4. Disposition of vibrational energy

We have seen that the photoexcitation step: \( ^1 \text{LC} \leftarrow S_0 \) is accompanied by IC to \(^1\text{MLCT}\). At a rigorous level of theory, in the absence of molecular rotation, all molecular eigenstates in this regime are eigenfunctions of vibronic symmetry, which survives breakdown of the Born-Oppenheimer approximation [56]. However, each of these eigenstates contains only a modest amount of \(^1\text{LC}\) electronic character, because the latter is diluted through the large density of vibrational states of the lower electronic manifold(s). Thus, as a practical matter, it is safe to assume that the system evolves to one of \(^1\text{MLCT}\) vibrational excitation. Likewise, the \(^1\text{MLCT} \rightarrow T_1\) transition that takes place via ISC also leads to mainly vibrational excitation within the \(T_1\) manifold. Thus, the \(^1\text{LC} \leftarrow S_0\) photon energy minus the energy of the \(T_1\) electronic origin is taken as vibrational energy. Adding this to the photoexcited molecule's \(S_0\) vibrational energy gives its total vibrational energy.

Turning now to the vibrational energy present in \(S_0\), this is due to thermal population of vibrational levels at 490 K. In light of the fact that there are 177 vibrational degrees of freedom, there is considerable vibrational energy in \(S_0\). An accurate determination of this vibrational energy distribution is challenging. The distribution function for the total amount of vibrational energy consists of a delta function (at an energy equal to the photon energy minus the \(T_1\) electronic energy) added to the vibrational energy distribution given by a convolution involving the 177 vibrational degrees of freedom at 490 K. This distribution is determined and discussed in Paper II, which follows this one. The important point here is that essentially all of this vibrational energy is transported from \(T_1\) to the ion, regardless of the details of its distribution. It is in this sense that vibrational excitation is said to act as a spectator in the ionization step.
3.5. Comparison with electronic structure theory and previous work

In Paper II, a detailed theoretical study of the electronic structure of the Ir(ppy)$_3$ system, including several low-lying states of the cation Ir(ppy)$_3^+$, is presented [54]. Here, a few of these results are compared to the experimental findings to establish registry between the experimental and computational results.

<table>
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<th>$S_0$ (theory)</th>
<th>$S_0$ (expt)</th>
<th>$T_1$ (theory)</th>
<th>$D_0$ (theory)</th>
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<td>(d) (e) (f)</td>
<td>(a) (b) (a)</td>
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<td>2.088 2.071 2.132</td>
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<td>2.088 2.071 2.132</td>
<td>2.139 2.116 2.213</td>
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<tr>
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<td>1.345 1.361 1.331</td>
<td>1.34 1.36 1.34</td>
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<td>1.345 1.361 1.331</td>
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<td>1.40 1.42 1.395, 1.41</td>
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<td>1.41 1.42 1.40</td>
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<td>– – –</td>
<td>1.487 1.40 1.419, 1.473</td>
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</tbody>
</table>

(a) current work, (b) [24], (c) [32], (d) [57], (e) [58], (f) [14]

Table 1. Bond lengths (Å) for $S_0$, $T_1$, and $D_0$ states of Ir(ppy)$_3$.

Calculations were carried out for the AIE and for VIE's at the $S_0$ and $T_1$ geometries, yielding respective values of 5.86, 5.87, and 5.88 eV. The fact that there is little difference among these is not surprising, given the similar geometries of the $S_0$ and $T_1$ states of Ir(ppy)$_3$ and the Ir(ppy)$_3^+$ ground state, $D_0$, (Table 1) and the delocalized nature of the orbitals, i.e., the more delocalized the involved orbitals, the less likely it is that there will be a geometry change in going between the equilibrium structures of the electronic states. As mentioned earlier, Franck-Condon factors are expected to be nearly diagonal, where, in the present context, diagonal means $\langle mv_i|nv_k'\rangle = \delta_{mn}\delta_{ik}$, where $i$ and $k$ denote vibrational degrees of freedom such as normal modes, $m$ and $n$ denote numbers of quanta, and the prime denotes the ion. This presumes that the normal modes of the neutral and the ion can be paired such that a given normal mode applies to both the neutral and the ion. In other words, for a given normal mode, were one to look...
at the classical motions of the neutral and ion they would be essentially indistinguishable. This is a good assumption in the present system. Thus, our calculations place both the AIE and the VIE's (at $S_0$ and $T_1$ geometries) in the vicinity of 5.9 eV. This is in accord with the experimental upper limit of 6.4 eV, and with the calculation of Hay that places the VIE at 5.94 eV [32].

To examine the assumption that vibrational energy is transferred more-or-less intact upon photoexcitation of this system, the $^1$LC $\leftarrow S_0$ absorption spectrum was calculated with all $S_0$ vibrational excitation suppressed. Excitation is vertical from the $S_0$ equilibrium geometry. In this calculation, 130 excited states were included. Details are given in Paper II [54]. Figure 12 shows the correspondence between the calculated and experimental spectra. The shape of the experimental spectrum is reproduced, albeit with energy offset that is within the anticipated error bars of the methods employed.

![Figure 12. Ultraviolet absorption spectra of fac-Ir(ppy)$_3$. The calculated spectrum (red) was obtained from the stick spectrum by assigning to each stick a Gaussian FWHM of 0.43 eV. The experimental spectrum (black) was recorded at room temperature in dichloromethane. Peak and shoulder positions (vertical arrows) are in eV. All stick heights have been increased by the same constant factor for viewing convenience, and curve height has been adjusted such that the maximum absorptions are equal. The low-energy, low-intensity wing due to $T_1$ $\leftarrow S_0$ (2.56 eV) is absent in the calculated spectrum because SOC was not included.](image)

It was pointed out in Section 2 that we were unable to establish that 355 nm photoionization is a 2-photon process. Adding the 355 nm photon energy to the $T_1$ electronic energy yields 5.94 eV, which lies below the experimental upper bound of 6.4 eV, is close to our theoretical VIE and AIE values of approximately 5.9 eV, and is equal to the value calculated by Hay [32]. It may well be that our inability to establish the 355 nm photoionization fluence dependence is a reflection of this near coincidence. Thus, we conclude that the AIE is less than 6.4 eV and is most likely ~ 6 eV. The only other experimentally based ionization energy for this species places the VIE at 7.2 eV [33], which is incorrect. In defense of these authors, however, is the fact that their measurement was not direct, but an inference. Specifically, it was assumed that a peak at 7.2 eV in energy loss spectra (using incident electron energies of 14, 20, 30, and 50 eV) was due to ionization. Apparently this assumption needs to be reconsidered.
4. Summary

- A regime of single-frequency 2-photon photoionization has been established (i.e., below ~ 1 mJ cm\(^{-2}\), see Fig. 9), and it has been shown that the Ir(ppy)\(_3^+\) parent ion is, for all practical purposes, the only ion product throughout this regime despite the fact that the cation is formed with considerable vibrational energy. This is examined quantitatively in Paper II. Photoionization was also achieved using a single 193.3 nm (6.414 eV) photon, again yielding just Ir(ppy)\(_3^+\).

- An upper bound for the ionization threshold for gas phase Ir(ppy)\(_3\) has been estimated on the basis of complementary experiments. Central to interpretation of the experimental results is the reasonable assumption that Ir(ppy)\(_3\) vibrational energy is carried over, essentially intact, to its ion. The 2-photon experiments give a very conservative upper bound of 6.67 eV, while the 1-photon experiment gives an upper bound of 6.4 eV. The upper bound of 6.4 eV is consistent with the theoretical values obtained by our group of approximately 5.9 eV [54] and by Hay of 5.94 eV [32]. Thus, the AIE is estimated to be ~ 6 eV. The VIE's at the S\(_0\) and T\(_1\) equilibrium geometries are essentially the same as the AIE. A calculation of the Ir(ppy)\(_3\) absorption spectrum, in which vertical excitation from the S\(_0\) equilibrium geometry is assumed, supports the assumption that vibrational excitation is transferred essentially intact upon photoexcitation.

- The electrical efficiency of an OLED depends on the embedded molecule's T\(_1\) energy relative to its ionization energy in the solid host. For example the IE's and electron affinities (EA's) (HOMO and LUMO energies, respectively) of molecules in the light-emitting layer needs to be matched to the energy levels of the electrodes. The low value of ~ 6 eV for the ionization energy of isolated Ir(ppy)\(_3\) augurs well for this species and its close relatives.

- An undulation with spacing of ~ 270 cm\(^{-1}\) (33 meV) was observed in the Ir(ppy)\(_3^+\) yield spectrum. Possible origins include: (i) structured \(\sigma_1\) and smooth \(\sigma_2\) versus energy, and (ii) smooth \(\sigma_1\) and structured \(\sigma_2\) versus energy. In the case of the latter, competition between radiationless decay and ionization can play a role. Resolution of the mechanism awaits further experimental work.

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References

[8] excitons of organic host