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Time-resolved photoelectron spectroscopy of a dinuclear Pt(II) complex: Tunneling autodetachment from both singlet and triplet excited states of a molecular dianion

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Time-resolved pump-probe photoelectron spectroscopy has been used to study the relaxation dynamics of gaseous $[Pt_2(\mu-P_2O_5H_2)_4 + 2H]^{2^-}$ after population of its first singlet excited state by 388 nm femtosecond laser irradiation. In contrast to the fluorescence and phosphorescence observed in condensed phase, a significant fraction of the photoexcited isolated dianions decays by electron loss to form the corresponding monoanions. Our transient photoelectron data reveal an ultrafast decay of the initially excited singlet ${}^{1}A_{2u}$ state and concomitant rise in population of the triplet ${}^{3}A_{2u}$ state, via sub-picosecond intersystem crossing (ISC). We find that both of the electronically excited states are metastably bound behind a repulsive Coulomb barrier and can decay via delayed autodetachment to yield electrons with characteristic kinetic energies. While excited state tunneling detachment (ESETD) from the singlet ${}^{1}A_{2u}$ state takes only a few picoseconds, ESETD from the triplet ${}^{3}A_{2u}$ state is much slower and proceeds on a time scale of hundreds of nanoseconds. The ISC rate in the gas phase is significantly higher than in solution, which can be rationalized in terms of changes to the energy dissipation mechanism in the absence of solvent molecules. $[Pt_2(\mu-P_2O_5H_2)_4 + 2H]^{2^-}$ is the first example of a photoexcited multianion for which ESETD has been observed following ISC. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4940795]

I. INTRODUCTION

The development of the electrospray ionization source has allowed ready access to vacuum isolated molecular multianions¹—and to photoelectron spectroscopic studies thereof.^{2–6} One of the most interesting characteristic phenomena which can be observed for isolated multianions, M^{n-} , is spontaneous electron tunneling autodetachment to yield $M^{(n-1)-} + e^-$. Depending on the system, this can occur from ground⁷ and/or electronically excited states⁴—albeit at widely different rates.

Multianions which are electronically metastable in their electronic ground states (i.e., characterized by negative electron affinities)⁸ can decay by this process on time scales which can range up to seconds as determined by the repulsive Coulomb barriers (RCBs) behind which the excess electrons are kinetically trapped.^{9,10} Autodetachment from electronically excited multianions is typically much faster and occurs on picosecond or even femtosecond time scales. This process was first demonstrated in a time-

resolved photoelectron spectroscopy (tr-PES) study of metal phthalocyanine tetrasulfonate tetraanions.⁴ More recently, it was also confirmed to be an important relaxation channel for the first singlet excited state (S_1) of the isolated bisdisulizole tetraanion ([BDSZ]⁴⁻)-a strong fluorophore in solution.¹¹ [BDSZ]⁴⁻, like the metal phthalocyanine based tetraanions is electronically metastable. However, excited state electron tunneling detachment (ESETD) can also occur for electronically stable multianions as recently shown both by the Verlet group^{12,13} and by several of us.¹⁴ Three criteria must be fulfilled for ESETD to be observable: (i) the energy of the tunneling state should lie above the detachment energy of the starting multianionic species, (ii) this excited state energy should be slightly below the RCB maximum and (iii) there should be no other significantly faster decay processes. ESETD is easily recognizable in one-photon PE spectra by a dominant constant electron kinetic energy (EKE) featureover a wide range of detachment energies.

All known ESETD examples are good fluorophores in solution—emitting out of their long-lived S_1 singlet excited states. When the corresponding isolated molecular multianions are photoexcited, they instead decay predominantly (and more rapidly) out of S_1 by ESETD. This raises the

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question whether there are multianions which can also undergo measurable ESETD from another spin manifold—after ultrafast intersystem crossing (ISC)? Here we demonstrate that $[Pt_2(\mu-P_2O_5H_2)_4 + 2H]^{2-}$, derived by protonation of the well-known inorganic luminophore $[Pt_2(\mu-P_2O_5H_2)_4]^{4-15-22}$ is such a system. It can undergo ESETD from both its first singlet excited state and from its lowest lying triplet state when isolated in the gas phase. We show this by one-color photoelectron spectroscopy (PES) and, in particular, by two-color femtosecond time resolved pump-probe photoelectron spectroscopy.

The unusual photophysical and photochemical properties of this binuclear d⁸-d⁸ diplatinum complex have so far only been studied in condensed phases, including ultrafast spectroscopy.²¹ In solution and solid state, the main UV/vis absorption feature of the $[Pt_2(\mu-P_2O_5H_2)_4]^{4-}$ chromophore is a strong metal-centered ${}^{1}A_{2u} \leftarrow {}^{1}A_{1g}$ transition near 370 nm,¹⁷ which is associated with a significant shortening of the $Pt \cdot \cdot Pt$ distance.^{19,20} The resulting singlet excited state can decay into a long-lived ³A_{2u} triplet state by efficient ISC.²² In solution, both the ${}^{1}A_{2u}$ and in particular the ${}^{3}A_{2u}$ state luminesce measurably. Despite the presence of two heavy platinum atoms with large spin-orbit coupling constants, the ISC rate turns out to be rather slow in condensed phase ($\tau_{ISC} = 10-30$ ps) and is strongly solvent-dependent. Understanding the effects which govern the spin dynamics of transition metal complexes like $[Pt_2(\mu-P_2O_5H_2)_4]^{4-}$ is one of the most interesting present challenges of ultrafast spectroscopy in condensed phase.²³

Optical probes of transition metal complexes in solution can be complicated by redox chemistry which leads to the simultaneous presence of species in different charge states and with different numbers/types of complexed counterions. For the system of interest here, this can lead to the superimposed contribution of various molecularly discrete diplatinum chromophores-an issue which can be addressed by probing mass-to-charge selected species in gas phase. Here, we have used this approach to study relaxation dynamics in the $[Pt_2(\mu-P_2O_5H_2)_4 + 2H]^{2-}$ dianion, which in the following we abbreviate as $[PtPOP + 2H]^{2-}$ and whose molecular structure is schematically shown in the inset of Fig. 1. Note that the negative excess charges are located on the pyrophosphate ligand backbone while both of the central Pt atoms have a formal oxidation state of +II. The current study is part of a systematic effort to understand the decay dynamics of *isolated* $[PtPOP + X, Y]^{2-}$ species (X, Y = H, K, Ag, ...) i.e., as a function of the cooperative interactions associated with counterion complexation. A complementary study of the fragmentation pathways as induced both by collisions and by UV photoexcitation has recently been published.²⁴

II. EXPERIMENTAL METHODS

A. Ion source

The potassium salt of tetrakis(μ -pyrophosphito) diplatinate(II) ([PtPOP + 4K]) was made from K₂PtCl₄ and H₃PO₃ following a procedure described in the literature.²⁵ Mass and charge selected ion beams of species based



FIG. 1. Stationary (one-photon) photoelectron spectra for electrosprayed $[PtPOP + 2H]^{2-}$ recorded at various detachment wavelengths as indicated (see text for details). Spectra were recorded using either magnetic bottle (MB-PES II (fs laser) and MB-PES I (ns laser)) or velocity map imaging spectrometers (VMI-PES (ns laser)). With the exception of a VMI-PES measurement of ions at 4.4 K (blue line) all spectra were recorded for dianions near room temperature. Spectra are plotted versus electron kinetic energy. Note constant kinetic energy features at 0.63 ± 0.05 and 0.97 ± 0.05 eV. Inset: minimum energy geometry of [PtPOP+2H]^2- based on DFT calculations²⁴ (black—Pt, red—O, yellow—P, white—H).

thereon were generated using electrospray ionization. $[PtPOP + 2H]^{2-}$, the isolated ion of interest here, was obtained by electrospraying a 1 mM solution of [PtPOP + 4K] dissolved in a mixture of acetonitrile/water (4:1). In order to avoid oxidation of the central Pt(II)Pt(II) moiety, it was necessary to use an acidic stock solution obtained by adding small amounts of acetic acid. The composition of the mass-selected ionic species studied by tr-PES was confirmed by high resolution mass spectrometry using a LTQ Orbitrap (see Fig. S1²⁶).

B. Magnetic bottle photoelectron spectroscopy

At KIT, measurements were performed on near-room temperature ions using two separate magnetic bottle PES (MB-PES I and II) machines each of which has been previously described.^{27,28} Both machines were equipped with magnetic bottle spectrometers which have an electron kinetic energy (KE) resolution (Δ KE/KE) of ~5% for electrons around 1 eV. In this study, MB-PES I was used for single-photon PES at wavelengths of 355, 266, and 213 nm-as provided by a ns-pulsed Nd: YAG laser. MB-PES II was used primarily for fs time-resolved pump-probe PES. Corresponding femtosecond laser pulses were provided by an Er³⁺ fiber oscillator and a regenerative Ti: sapphire amplifier operating at a 1 kHz repetition rate (Clark-MXR, CPA 2001). The 775 nm fundamental and the 388 nm frequency doubled outputs were used as the probe and pump wavelength, respectively. The pulse duration was determined by a cross correlation

measurement in a thin beta-barium borate crystal to be 360 ± 20 fs (FWHM).

Tr-PES measurements constitute the bulk of the work reported here and we therefore provide some further details. The ion beam part of the experiment was synchronized with the 1 kHz laser system by accumulating the continuous output of the electrospray ion source in a cylindrical rf ion trap prior to pulsed extraction-to form the primary ion beam. For photoelectron spectroscopy, ions were perpendicularly extracted from this primary ion beam into a linear time-of-flight mass spectrometer (TOFMS) which was itself connected to a perpendicularly oriented magnetic bottle photoelectron spectrometer. To interface with the photoelectron spectrometer, the TOFMS drift tube contained a pulsed mass gate and a pulsed deceleration region (immediately downstream). The latter allows to slightly focus the selected/decelerated ions into the detachment region of the PE-spectrometer and at the same time to reduce Doppler broadening in the photoelectron spectra. After reaching the detachment region of the magnetic-bottle photoelectron spectrometer, ions were interacted with spatially overlapping pump and probe laser beams. These were incident perpendicular to both ion beam and spectrometer axis. Pump and probe laser beams were typically focused to diameters of 1 mm on the ion beam axis. Focused pulse intensities were ca. 1×10^{11} W/cm² for the fundamental (probe) and 4×10^{9} W/cm² for 388 nm (pump). Linearly polarized pump and probe pulses were delayed relative to each other with an optical delay line which allowed for delays of up to 100 ps. In order to directly determine time-dependent isotropic signal functions (independent of rotational dephasing), all tr-PES experiments were performed with the polarization vectors of the pump and probe laser beams set at the magic angle (= 54.7°) relative to one another-with the pump laser polarized along the electron spectrometer axis.

In several cases, fs pump laser irradiation was also used to record one-photon PE spectra. In particular, we studied the effect of systematically moving the pump laser focus a few mm "upstream" out of the PE spectrometer extraction volume. This allowed us to probe delayed electron emission processes occurring on the 100 ns time scale following pump laser irradiation, corresponding to the flight time of ion packets between the point at which they were irradiated to the spectrometer interaction region.

C. Velocity map imaging (VMI) photoelectron spectroscopy

Several single-photon PES measurements were performed at Brown University using a VMI-PES apparatus²⁹ equipped with a variable temperature cryogenic ion trap.³ The [PtPOP + 2H]^{2–} doubly charged anions were produced using a ESI source and were stored in the ion trap, which could be operated from room temperature down to 4.4 K. The tunable detachment wavelengths in the range of 346.57-361.04 nm were provided by the frequency doubled output of a dye laser. For the current study, the VMI apparatus had an electron KE resolution (Δ KE/KE) of ~3% for electrons around 1 eV, as was calibrated by the known spectrum of Au[–].

III. RESULTS AND DISCUSSION

A. Stationary photoelectron spectra

Figure 1 shows one-photon photoelectron spectra obtained for $[PtPOP + 2H]^{2-}$ at three detachment wavelengths ranging from 354.85 to 388 nm. The photoelectron spectra were obtained on MB-PES I and II and VMI-PES machines as indicated. They are plotted versus EKE. Note that all spectra have a common detachment feature at an electron kinetic energy of 0.97 ± 0.05 eV. The two VMI-PES measurements shown (354.84 nm) were obtained at two different vibrational temperatures as set by the Paul pretrap. Cooling to a nominal temperature of 4.4 K reduces the width of the recorded spectral feature while the EKE of the band maximum remains constant. Further VMI-PES measurements obtained over a wider detachment wavelength range (346.57-361.04 nm) are shown in Fig. S2.²⁶ These confirm the presence of a common detachment feature at EKE of 0.97 eV independent of the UV detachment wavelength used. Irradiation in this spectral window is associated with a platinum centered ${}^{1}A_{2u} \leftarrow {}^{1}A_{1g}$ transition to form the first singlet excited state-as well-known for PtPOP complexes in solution and as also recently inferred to occur for isolated $[PtPOP + 2H]^{2-}$ in gas phase on the basis of photo-induced dissociation measurements (see also Fig. S3²⁶).²⁴ Following our previous work and also the work of the Verlet group, we attribute the 0.97 eV constant EKE feature observed in the PES measurements of $[PtPOP + 2H]^{2-}$ to ESETD—from the ${}^{1}A_{2u}$ excited state, which for simplicity we denote as " S_1 " from now on. Since there is no evidence for direct detachment in the spectrum at 354.84 nm, we estimate a lower bound for the inner RCBs height of 3.5 eV.

From measurements with higher photon energies which allow for direct detachment over the top of the repulsive Coulomb barrier, we could also determine the adiabatic detachment energy (ADE = 2.2 eV) and confirm the value for the inner RCB of 3.5 eV. The corresponding one photon PE spectra obtained at 266, 258, and 213 nm are shown in Fig. S4.²⁶

Returning to Fig. 1, we note that there is an additional detachment peak at an EKE of 0.63 ± 0.05 eV in the 388 nm spectrum which is also present in the 355 nm spectrum (although with a different relative intensity). Again the constant EKE nature of this spectral feature indicates a tunneling detachment process. A potential precursor state for these lower energy electrons is the known ${}^{3}A_{2u}$ triplet state of the PtPOP molecule. We denote this state as "T₁." More evidence for this assignment will be given in Secs. III B–III F.

Surprisingly, the T_1 feature is completely absent in the velocity map imaging measurement obtained at approximately the same detachment wavelength of 354.84 nm and similar photon fluences. We attribute this discrepancy to a delayed detachment character of the T_1 feature and in particular to differences in the sensitivity of the two types of spectrometers (magnetic bottle- and VMI-PES) to delayed electron detachment processes occurring on a >100 ns time scale after irradiation. We will return to this point below.

B. Delayed detachment

The inference that the T₁ feature observed in the MB-PES is associated with delayed electron detachment is supported by further measurements shown in Fig. 2. This figure displays one-photon PE spectra recorded at the same detachment wavelength for several irradiation positions-starting from the near-optimum location at the center of the interaction zone (bottom in Fig. 2) and systematically moving the laser focus upstream from this position along the incoming ion beam. To highlight the effect, the spectra are plotted against *electron* flight time (i.e., raw data before the Jacobi transformation necessary for conversion onto an energy scale). Superimposed on the spectra are schematics of the corresponding laser position relative to the cylinder axis of the perpendicularly oriented spectrometer. It was possible to move the laser beam focus upstream by about 1.5 mm before hitting the laser baffle. The S_1 peak maximum decreases in relative intensity and quickly disappears completely as the laser beam focus is moved progressively further upstream. In contrast, the relative intensity of the T₁ feature grows. Moreover the flight time of the T₁ feature at peak maximum increases by 600 ns when the laser is focused to its outermost position (furthest "upstream"). Note that $[PtPOP + 2H]^{2-}$ ions with a kinetic energy of ca. 30 eV would travel a distance of 1.5 mm in this time frame, thus matching our expectation for the kinetic energy of the decelerated ion beam.

Reference measurements on comparably decelerated monoanion species which are known to only undergo direct detachment confirm that no electrons can be seen if the detachment laser is positioned 1.5 mm upstream of the spectrometer axis. Correspondingly, we interpret the measurements shown in Fig. 2 as indicating that S_1 electrons must be produced very shortly after irradiation in order to be detected, whereas T_1 electrons *are still being emitted by*



FIG. 2. Photoelectron spectra vs. electron time of flight as recorded at a fixed detachment wavelength of 388 nm for three different positions of the perpendicularly incident detachment laser (as schematically indicated (x)). The bottom spectrum corresponds roughly to the standard laser position as optimized for detection of directly detached electrons. Two broad detachment features comparable to those of Fig. 1 are apparent. Upon moving the laser beam upstream, the feature attributable to fast detachment is rapidly lost whereas the second feature becomes relatively stronger and shifts by 600 ns to longer times. This reflects delayed electron detachment on a >100 ns time scale.

photoexcited multianions which have travelled for >100 ns before entering the spectrometer extraction region.

Note that the missing T_1 feature in VMI spectra is consistent with our inference of significantly delayed detachment. The VMI apparatus was designed for highresolution PES of directly emitted photoelectrons.²⁹ The directly emitted electrons are promptly accelerated out of the interaction zone to the imaging detector. Significantly delayed emission would lead to spectral blurring.

C. Tr-PES spectra

So far, we have inferred two different ESETD pathways from one-photon PE spectra of gas phase $[PtPOP + 2H]^{2-}$ mainly based on knowledge that stems from condensed phase measurements. To study the short time scale dynamics of energy redistribution in isolated $[PtPOP + 2H]^{2-}$ after excitation to its S₁ state, we performed tr-PES measurements with 388 nm pump and 775 nm probe photons—at systematically varied pump-probe delay times. Figures 3(a) and 3(b) show the corresponding pump-probe PE spectra as a function of electron kinetic energy. In all cases, the spectra shown are *difference spectra*, i.e., for each pumpprobe spectrum, a reference spectrum obtained with just the 388 nm pump wavelength was measured and subtracted



FIG. 3. Time resolved photoelectron difference spectra of isolated [PtPOP +2H]²⁻ for systematically varied delays between 388 nm pump and 775 nm probe laser beams: (a) contour plot showing an overview of the spectra for the full electron kinetic energy and delay time range studied; (b) vertical cuts through the contour diagram at three pump-probe delays to highlight the major features of the ultrafast dynamics (raw pump-probe data in inset). Features at EKE < 1.3 eV are related to tunneling electron loss while features at higher EKE stem from pump-probe detachment.

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(the inset of Fig. 3(b) shows raw pump-probe data before such subtraction). As a result, only the transient features remain visible. The contour diagram shown in Fig. 3(a) visualizes the full dataset obtained. Additionally, Figs. 3(b) and 4 highlight selected spectral information by showing vertical cuts through the contour diagram at various pumpprobe delays. At first glance, two phenomena are particularly noteworthy: (i) depending on delay, we observe two strong two-color photoelectron signals occurring in the EKE range 1.3–2.9 eV while the region of the tunneling detachment signal (both S₁ and T₁ ESETD features) becomes correspondingly bleached and (ii) the transient feature at 2.45 eV builds up immediately and decays rapidly whereas the feature at 1.8 eV grows in more slowly and then remains constant out to the longest pump-probe delay times of 100 ps accessible in our experiment.

Before going on to discuss the time-resolved measurements, it is important to realize that now two fundamentally different detachment mechanisms contribute to the observed photoelectron spectra. Features in the ESETD region are related to delayed excited state tunneling through the Coulomb barrier. In contrast, features in the pump-probe region originate from instantaneous direct detachment given that the sum of the pump and the probe pulse energy is sufficient to overcome the top of the RCB (see also Section III E and Fig. 6).

Next, we provide a more detailed analysis of the tr-PES data. First of all, there are no transient features at negative delay times (t < t₀), i.e., when the 775 nm probe arrives before the 388 nm pump pulse. The red curve shown in Fig. 3(b) (at a pump-probe delay of 200 fs) exhibits a main feature at 2.45 eV corresponding to probe pulse induced electron detachment from the initially populated lowest singlet (S₁) excited state of [PtPOP + 2H]²⁻. Over the next 2 ps, the population of this state rapidly decays and a second peak builds up at 1.8 eV (blue curve). To investigate the connection between this long-lived lower energy feature and the S₁ detachment signal, Fig. 4 highlights the processes occurring on the earliest time scale after photoexcitation—as measured in the two-photon pump-probe region of the PE spectra.

Fourteen transients measured in a sequence of narrow time steps show the interconversion of the population from



FIG. 4. Fourteen transients measured in a sequence of narrow time steps $(9 \times 100 \text{ fs} \text{ followed by } 4 \times 250 \text{ fs})$ during the first 2.2 ps after photoexcitation. Dashed arrows indicate that populations increase/decrease with time.

the 2.45 eV S₁ to the lower lying 1.8 eV state with the occurrence of an isosbestic point at 2 eV. We conclude that the latter state is the T₁ triplet state of $[PtPOP + 2H]^{2-}$, which we already put forward to explain the delayed tunneling electron emission feature observed in the one-photon PE spectra. The observability of an isosbestic point gives valuable information about the states participating in the intersystem crossing process: there are no spectral shifts caused by relaxation processes in the respective excited states (e.g., IVR) and there is no evidence for the involvement of an (additional) intermediate electronically excited state.

Note that after 2.2 ps, there is still some intensity left at 2.45 eV which apparently does not contribute to a further growth of the 1.8 eV triplet peak. A certain subpopulation of the initially excited $[PtPOP + 2H]^{2-}$ molecules seems not to undergo ISC but instead to decay via other channels.

Besides the pump-probe two-photon detachment, the appearance of negative intensities in the kinetic energy range of the ESETD features from 0.3 to 1.3 eV is particularly noticeable (Fig. 3(b)). The probe pulse depopulates the precursor states of delayed electron emission and therefore causes the observed transient ESETD bleaching. Crucially, both the singlet and triplet tunneling features are bleached which provides experimental evidence that the S₁ and T₁ states probed are in fact the excited states responsible for the tunneling emission.

At high electron kinetic energies, >2.8 eV, some additional (weaker) transient features are observed. They result from ionization out of the S_1 and T_1 excited states by two probe photons as a consequence of focusing the probe laser beam during the measurements (necessary to obtain sufficient signal-to-noise ratio in the transient ESETD bleaching region).

D. Kinetic analysis of transients

Next, we evaluate the transients shown in Fig. 3 towards obtaining the corresponding kinetic parameters. Fig. 5(a)shows fits to spectral signatures as obtained by integrating the intensities of difference spectra over specific kinetic energy ranges-to highlight the dynamics of the four characteristic features. These are the ranges corresponding to S_1 and T_1 pump-probe ionization as well as S_1 and T_1 transient ESETD bleaching, respectively. Note that these features partially overlap spectrally. More accurate state-specific kinetic information can be obtained by explicitly taking such overlap into account by way of "decay associated difference" spectra (DADS). For a comprehensive evaluation of our time resolved data, we therefore employed a global fitting routine based in part on the open-source software package Glotaran.³⁰ Within this approach, the temporal evolution of the transient features is fitted with a fixed number of time constants optimized to simultaneously describe the full (3D) dataset. Additionally, the method allows us to disentangle the overlapping spectra of the excited states involved-based on their specific dynamic behavior. These DADS spectra are particularly useful when the excited state signatures show no time-dependent spectral shifts (e.g., if vibrational energy redistribution leads only to negligible changes to the Franck-Condon factors governing ionization). Our measured



FIG. 5. Kinetic evaluation of the transients shown in Fig. 3: (a) integrated intensities (open circles) over specific kinetic energy ranges as indicated together with their fit functions (solid lines)—to highlight the dynamics of the four characteristic features seen in the difference spectra and (b) decay associated difference spectra (DADS) as determined in a best fit to the data (with three time constants) using the Glotaran software package.³⁰

transients indicate that this condition is exceptionally well met in the $[PtPOP + 2H]^{2-}$ system.

The fit function has the following form:

$$f(E_{kin},t) = \sum_{i} A_i(E_{kin}) \left(\exp\left(-\frac{t}{\tau_i}\right) * irf(t,t_0,t_p) \right).$$

It sums up i monoexponential decay functions (each having a characteristic time constant τ_i) convoluted with the Gaussianshaped instrumental response function (t₀: time zero, t_p: pulse duration) and multiplied with their corresponding DADS (A_i).

Using this approach, we find that the transients shown in Fig. 3 can be best fit with *three* time constants: $\tau_1 = 680 \pm 100$ fs, $\tau_2 = 2.5 \pm 0.5$ fs, and $\tau_3 = \infty$ (>100 ns).

The three DADS corresponding to these three time constants are shown in Fig. 5(b). Positive intensities belong to features which decay with the respective time constant, while negative intensities belong to features which increase correspondingly. As Fig. 5(b) demonstrates, the same time constant of $\tau_1 = 680 \pm 100$ fs (black curve) connects the decaying S₁ (2.45 eV) and increasing T₁ signals (1.8 eV). Clearly, τ_1 describes the time scale of the ISC process—to first order. In addition, the initially observed bleaching of the S₁ ESETD region (1.0 eV) (negative intensity in the difference spectra) disappears over time, as shown in Fig. 5(a). This process is partially characterized by time constant τ_1 in the corresponding DADS. The end of transient ESETD bleaching marks the point in time where the S₁

population has already completely decayed via tunneling (and ISC) prior to the interaction with the probe pulse. Consequently, we infer from the τ_1 DADS the presence of ultrafast S₁ ESETD during the first 680 fs after photoexcitation.

Note that there is a second time constant of 2.5 ± 0.5 ps involved in the decay of the S₁ pump-probe detachment feature as shown in the red curve. τ_2 also contributes significantly to the S₁ tunneling feature as indicated by the corresponding DADS component at 1.0 eV. However no clear signals are observable in the kinetic energy region of the spectrum related to the T₁ triplet state. τ_2 characterizes a subpopulation of S₁ which does not undergo ISC but solely decays via ESETD on a few ps time scale—as already mentioned when discussing Fig. 3(b).

We cannot quantify the third time constant τ_3 with our pump-probe spectroscopy measurements. All features in the DADS corresponding to τ_3 (blue curve) remain constant within our experimentally accessible delay range. There is no decay of the T₁ pump-probe ionization signal at 1.8 eV or any cessation of the triplet tunneling bleaching at 0.65 eV. Interestingly, this also implies that on our tr-PES time scale (100 ps) the major amount of T₁ ESETD electrons have yet to be emitted.

Based on our delayed detachment measurements, we estimate the lifetime of the T_1 state to be at least on the order of several hundreds of nanoseconds.

Again three-photon processes (pump + 2 probe photons) are observable at kinetic energies >2.8 eV in the τ_1 and τ_2 DADS and already at energies >2.4 eV in the τ_3 DADS. Note that analogous measurements using an unfocused probe laser beam (Fig. S5²⁶) yielded time constants which are identical to those shown in the table within error.

We therefore conclude that the following elementary processes contribute to the decay dynamics of $[PtPOP + 2H]^{2-}$ when photoexcited into its S₁ state:

S_1	τ_1	T ₁	(ISC)
	\longrightarrow	monoanion + e	(electron tunneling from S_1)
S_1	$\xrightarrow{\tau_2}$	monoanion + e	(electron tunneling from S_1)
T_1	$\xrightarrow{\tau_3}$	monoanion + e	(electron tunneling from T_1)

Luminescence and internal conversion are potential competing relaxation mechanisms which are not included in the above diagram. In solution, however, the main process depopulating the S_1 state is ISC with an almost unit quantum yield.²² It therefore seems likely that in gas-phase fluorescence or internal conversion are also not competitive—particularly as S_1 -ESETD and ISC are found to be so fast. In contrast, it is conceivable that phosphorescence out of the long-lived triplet excited state could occur in parallel to T_1 ESETD. Future trapped ion laser induced photoluminescence measurements would help to resolve this issue.³¹

Based on the intensities in the 2.45 eV region of the DADS, we can estimate the relative amplitudes of the decay channels depopulating the S₁ state. Roughly, 1/3 of the photoexcited species decays via S₁ ESETD on a time scale of $\tau_2 = 2.5$ ps while the other 2/3 of the excited molecules decay

on a 680 fs time scale. Both rapid ISC and a smaller amount of fast S₁ ESETD contribute to τ_1 . Within the scope of this paper, we cannot completely disentangle the two processes but estimate that a dominant part of the τ_1 subpopulation decays by ISC. We will address the nature of the driving force for ISC in [PtPOP + 2H]²⁻ in Section III F.

E. Energy conservation

Based on the results presented above, we propose a modified Jablonski-type diagram to describe the photophysics of gas phase $[PtPOP + 2H]^{2-}$ (Fig. 6) and next discuss the associated energetics, an issue which we have so far neglected. Under isolated conditions and on our experimental time scale, the energy deposited into the molecule via pump and probe laser beams is either partially released by photoelectron emission (whose kinetic energies we measure) or remains within the molecule. As already pointed out above, other channels like luminescence or fragmentation are unlikely to be kinetically competitive and are excluded to first order.

For better clarity, Fig. 6 is divided into two parts focusing on processes associated with (a) the S₁ state and (b) the T₁ state, respectively. Note that the vibrational ground state energies of S₁ and T₁ states are taken from measurements of [PtPOP]^{4–} complexes in solution.²¹ As recently shown,²⁴ the photoinduced dissociation spectrum of isolated [PtPOP + 2H]^{2–} in the range of the ${}^{1}A_{2u} \leftarrow {}^{1}A_{1g}$ transition closely matches the absorption spectrum of the [PtPOP]^{4–} chromophore in solution (also consistent with the fact that [PtPOP]^{4–} shows very little solvatochromism).¹⁷ With a pump photon energy of 3.2 eV as used in our experiments, we should therefore be resonantly exciting the [PtPOP + 2H]^{2–} ions at the red edge of the ${}^{1}A_{2u} \leftarrow {}^{1}A_{1g}$ absorption band (see also Fig. S3).²⁶

Interestingly, we observe that the S_1-T_1 energy difference, as determined from the peak maxima of the corresponding ESETD features, deviates from the splitting derived from the pump-probe transients. In the latter case, the splitting amounts to 0.65 eV ($S_1 \rightarrow 2.45$ eV and $T_1 \rightarrow 1.8$ eV) whereas it is only 0.35 eV for ESETD ($S_1 \rightarrow 1.0$ eV and $T_1 \rightarrow 0.65$ eV). We explain this discrepancy as follows:

- (1) Pump-probe ionization involves a vertical transition from the dianions excited state to the singly charged anions ground state. For this instantaneous photodetachment over the top of the RCB, the position of the two-photon peak maximum is determined by Franck-Condon factors connecting the dianion excited states to the monoanion final state.
- (2) Tunneling emission through the RCB is a delayed process which is considered to conserve the vibrational excitation level of the molecule during electron emission.³²

As Fig. 5(a) shows the measured EKE of the electrons generated by S_1 tunneling (1.0 eV) is perfectly consistent with the molecule's adiabatic electron binding energy, i.e., it fits very well a transition from the S_1 state at 3.2 eV to a [PtPOP + 2H]⁻ monoanion at 2.2 eV. Autodetachment from the bottom of the S_1 potential curve yields monoanions which are vibrationally cold with respect to the reaction coordinate.

Direct pump-probe ionization is associated with a vertical detachment energy of roughly 2.35 eV. This is 0.15 eV larger than the ADE, which must primarily reflect the fact that the resulting $[PtPOP + 2H]^-$ monoanion has a significantly different equilibrium geometry. In the S₁ state of $[PtPOP + 2H]^{2-}$, the valence orbital has binding character so an elongation of the central Pt–Pt bond is expected following the ionization.

Ionization processes out of the T_1 state are strongly influenced by the fact that ISC from S_1 is associated with redistribution of the singlet-triplet energy gap (ca. 0.7 eV) from electronic to vibrational degrees of freedom (presumably initially deposited into quanta of the Pt(II) \leftrightarrow Pt(II) stretching vibration). As Fig. 5(b) indicates, vertical pump-probe



FIG. 6. Jablonski-type diagrams illustrating the energetics and processes relevant for this study. For clarity, processes associated with (a) the S₁ state and (b) the T₁ state are shown separately. S₁ \leftarrow S₀ excitation at 3.2 eV (pump) is followed either by S₁—ESETD or by ISC. The latter yields highly vibrationally excited T₁ which undergoes delayed T₁-ESETD. The ESETD steps yield electrons with kinetic energies of 1.0 (S₁) and 0.65 eV (T₁), respectively. The corresponding excited state dynamics was followed by 1.6 eV (probe) irradiation yielding detached electrons at 2.45 (S₁) and 1.8 eV (T1).

transitions out of T₁ (again reflecting the pertinent Franck-Condon factors) lead to hot ground state monoanions 0.8 eV above the ADE. By contrast, triplet autodetachment (in our experimental time window) results on average in $[PtPOP + 2H]^{-}$ monoanions 0.35 eV above the ADE. This difference reflects only partial conservation of $Pt(II) \leftrightarrow Pt(II)$ vibrational excitation during significantly delayed electron emission.

We conclude that the initial amount of internal energy in the precursor state affects the two tunneling emission channels under consideration in a very different way. Tunneling emission from the long-lived T_1 state proceeds significantly further outside the Franck Condon region than the S₁ state ESETD.

F. Comparing the photophysics of [PtPOP + 2H]²⁻ in the gas phase with that in solution

Since the first synthesis of PtPOP-based complexes in 1977,³³ their condensed phase photophysics has attracted considerable and ongoing attention. Especially their ISC dynamics are not entirely understood. In this context, it is of interest to compare our results for isolated $[PtPOP + 2H]^{2-}$ with a recent fs transient absorption and fluorescence upconversion study of [PtPOP]⁴⁻ photoexcited into its S₁ state in solution at room temperature.²¹ The vertical S_0 to S1 excitation is associated primarily with changes to the bonding configuration of the central Pt(II) ··· Pt(II) dimer while the surrounding pyrophosphate groups act essentially as spectators. As the corresponding ${}^{1}A_{2u}$ excited state has a significantly shorter dimer equilibrium distance than the ${}^{1}A_{1g}$ ground state, this causes immediate vibrational excitation of the Pt(II) ··· Pt(II) moiety. The authors of Ref. 21 then observe rapid dissipation of this excess vibrational energy to the solvent on time scales <2 ps, followed by ISC on a time scale of 10-30 ps depending on the solvent. This is significantly slower than the ISC rate of 680 fs found in our tr-PES study. Apparently, the excited states photophysics are remarkably strongly influenced by the PtPOP molecules local environment. Based on what is known from literature, we propose two (partially interdependent) mechanistic schemes to account for the substantial acceleration of the ISC dynamics in the gas phase:

(1) Nascent ${}^{1}A_{2u}$ state species generated in the gas phase have no solvent molecules to transfer excess vibrational energy to. Dissipation only via coupling to the vibrations of the pyrophosphate framework is likely to be less efficient because of a reduced density of comparably low frequency vibrations (the $Pt \cdot \cdot \cdot Pt$ stretch vibration in both $^1A_{2u}$ and $^3A_{2u}$ states is ca. 150 $\text{cm}^{-1\,16,18}\text{)}.$ If the ISC rate scales with dimer vibrational excitation, then closing the "dissipation-to-solvent" channel would be expected to lead to faster ISC. By the same token, our inference of two different S1 populations, only one of which undergoes predominantly ISC (see Section III E), indicates that τ_{isc} depends more strongly on Pt. . . Pt vibrational excitation than does $\tau_{ESETD(S1)}$. Or to put it another way, gas-phase ¹A_{2u} species decay predominantly by either S₁-ESETD or T₁-ESETD depending on their initial $Pt \cdot \cdot Pt$ vibrational

excitation level. The gas phase photofragmentation study of Kruppa et al. provides further support for this picture.²⁴ Towards the high energy side of the S₁ photodissociation band, the relative cross section for electron emission is found to decrease whereas fragmentation by loss of neutrals becomes more prominent. Presumably, such photofragmentation occurs by way of the long lived T_1 state formed via ISC. For sufficient excitation energy, the latter process becomes kinetically favored compared to S1 ESETD.

Further gas-phase measurements at variable pump photon energies (and initial vibrational temperatures) would be desirable in order to explore the extent to which the ISC rate depends on vibrational excitation level. Note however that excitation energy dependent studies in solution by the authors of Ref. 21 did not in fact yield faster ISC rates able to compete with the 2 ps "dissipation-to-solvent" channel. Therefore, additional aspects of solvent-solute interaction apparently need to be considered in order to explain the large observed variations in ISC rates.

(2) Recent experimental and theoretical studies^{34,35} have investigated the impact of ligand backbone rigidity on ISC rates in solvated PtPOP complexes. Towards this end, a significantly more rigid version of the PtPOP molecule was synthesized by bridging the pyrophosphate ligands with BF_2 units. Upon photoexcitation into its S_1 state (in solution), the resulting derivative manifests slower radiative decay and a reduced ISC rate compared with the unmodified complex. For both the derivative and the unmodified complex, the ISC rate was also observed to be strongly temperature dependent.^{34,36} The authors conclude that a symmetry breaking structural distortion is essential for efficient ISC-as mediated by spin-orbit coupling between the ${}^{1}A_{2u}$ and ${}^{3}A_{2u}$ states. For $[PtPOP + 2H]^{2-}$, the energy required for such a distortion will be higher in the presence of a "retaining" solvation shell. Conversely, large amplitude motion of the ligand backbone is easier to excite in the gas phase, potentially leading to faster ISC rates. Dynamical simulations would help to quantify these effects.

IV. CONCLUSION

We have studied the decay dynamics of mass-selected gaseous $[PtPOP + 2H]^{2-}$ ions upon photoexcitation into its ${}^{1}A_{2u}$ (S₁) state—by means of time resolved pump-probe photoelectron spectroscopy. The primary energy dissipation channel is delayed electron loss to form the corresponding monoanion, $[PtPOP + 2H]^{-}$. Interestingly, this takes the form of two ESETD processes, each leading to the emission of electrons with characteristic kinetic energies. Specifically, these two ESETD channels correspond to detachment from the S₁ state (on a time scale of several ps) and significantly slower detachment from the T_1 state (on a >100 ns time scale) after rapid ISC. Compared to solution studies of the PtPOP chromophore at room temperature, we find a significantly faster ISC rate in the gas phase $(680 \pm 100 \text{ fs})$ vs. 10-30 ps). This can be rationalized in terms of missing

solvent molecules and concomitant changes to the dissipation of initially excited $Pt \cdots Pt$ dimer vibrations. The observed correlation between structure, environment, and excited state dynamics in PtPOP complexes can be investigated further in gas phase. Specifically, experiments with mass selected ions allow for controlled modification of the species probed via counter ion exchange. Using this approach we have also studied isolated $[PtPOP + X, Y]^{2-}$ species X, Y = H, K, Ag. Results will be presented in a future publication.

This is the first report of excited state electron tunneling out of a triplet state following the photoexcitation of a singlet ground state chromophore. In the future, we intend to further characterize how the phenomenology of triplet tunneling differs from S_1 ESETD. For instance, it would be interesting to compare the corresponding heights and shapes of the repulsive Coulomb barriers (RCB(S_1) and RCB(T_1)).

Overall, ESETD offers a useful new way of studying energy flow, intersystem crossing, and dissipation in isolated luminophores (that can be prepared as multiply negative ions with their excess electrons remote from the chromophore moiety).

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