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Excited-state energetics and dynamics of zinc tetrabenzoporphine in supersonic expansions

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precursor in both Dabco and acetylene. The nature of this precursor is not clear. In the case of the simplest molecule, C_2H_2 , the precursor can be an excited singlet state of the parent, a state of the C_2H radical, or an excited singlet (e.g., $C^1\Pi_g$) of C_2 itself. We find that the excited radicals are formed fast, the radical fluorescence risetime is the same as that of the laser pulse, and the dependence of the radical luminescence on parent molecule pressure is linear, indicating a noncollisional radical production sequence. The enhancement by Xe, however, is observed even at low pressure (~ 1 torr). An enhancement of the $a^3\Pi_u \rightarrow X^1\Sigma_g^+$ intersystem crossing in C_2 by Xe at low pressures has been reported recently.^{1,2} However, unlike the case of the metastable $\tilde{a}^3\Pi_u$ state, the precursor resulting in the formation of $\tilde{d}^3\Pi_u$ state must be short lived. The observation of strong enhancement even at low pressures is therefore somewhat puzzling.

A second type of interpretation involves the effect of the laser light on Xe itself. Xe does not exemplify linear absorption at 248 or 193 nm; however, under our focused beam conditions near two-photon resonant, three-photon ionization at 248 nm and two-photon ionization at 193 nm ($IP(Xe) \approx 12$ eV) take place. In an earlier study of the multiphoton photolysis of CO^{11} at 193 nm, it was reported that the $C(3^3P^0 \rightarrow 2^3P)$ emission was enhanced while the $C(3^1P^0 \rightarrow 2^1S)$ emission was quenched when Xe was introduced. It was assumed¹¹ that the spin-flipping collisional process $C(3^1P^0) + e^- \rightarrow C(3^3P^0) + e^-$ takes place, where the electrons are supplied by the two-photon nonresonant ionization of Xe at 193 nm. It is possible then that the behavior we have observed can be explained on the basis that the two-photon ionization of Xe at 193 nm is more efficient than three-photon ionization at 248 nm. The free

electrons have higher mobility than Xe and can induce efficient spin-flipping processes in the precursor or the C_2^* radical itself. It should be noted that, if the $\tilde{c}^1\Pi_g$ state (first singlet above $\tilde{d}^3\Pi_u$) of C_2 is the precursor of the $\tilde{d}^3\Pi_u$ state, the intersystem crossing will result in highly vibrationally excited ($v \geq 8$) $\tilde{d}^3\Pi_u$. Such excitation has not been observed even at the lowest pressures used.

Based on the cross-section data given in ref 12, about 10^{11} electrons/cm³ are produced by the ionization of Xe (10 torr) under our experimental conditions. Using a photoionization cell analogous to the one described in ref 13 we find that the ionization at 193 nm is a factor of 3 higher than the ionization at 248 nm under the laser power conditions employed here. It is not clear if the factor of three higher electron yield at 193 nm can account for the observed enhancement of the C_2^* emission. However, in addition to the total ion yield the energy of the electrons produced in the photoionization process, i.e., 0.7 eV at 193 nm and 2.9 eV at 248 nm, may be of importance. It is quite possible that the spin-flipping process has a higher cross section with the slower electrons because of a resonance scattering behavior.^{14,15}

In summary, we have demonstrated an unusual collisional enhancement of the $C_2^*(\tilde{d}^3\Pi_g)$ formation in multiphoton fragmentation processed by Xe "buffer" gas. The effect of Xe on the $C_2^*(^3\Pi_g)$ formation is excitation wavelength dependent. The observed effect is tentatively associated with a collisional enhancement, by Xe or free electrons, of a spin-forbidden process which results in $\tilde{d}^3\Pi_u$ state formation.

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Excited-State Energetics and Dynamics of Zinc Tetrabenzoporphine in Supersonic Expansions

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Laser-induced fluorescence excitation spectra of the zinc tetrabenzoporphine molecule in seeded pulsed supersonic expansions of He provide information on the electronic-vibrational level structure of the $S_0 \rightarrow S_1$ and the $S_0 \rightarrow S_2$ excitations. Electronic relaxation in the S_1 manifold was interrogated by time-resolved spectroscopy, while energy-resolved, line-broadening data provided semiquantitative information on interstate radiationless relaxation from the electronic origin of the S_2 state.

Introduction

An extremely interesting application of the techniques of laser spectroscopy of ultracold, isolated, large molecules in supersonic expansions¹ will involve the investigation of

electronically-vibrationally excited states of large molecules, which are relevant for the elucidation of basic photobiological processes. In this context, the interrogation of the excited-state level structure and radiationless transitions of "isolated" porphyrins are of considerable interest. The work of Fitch et al.² on the Q_x and Q_y bands of the phthalocyanine molecule in supersonic expansions

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provided a significant step in that direction. We have undertaken recently a study of excited-state energetics and dynamics of the lowest-lying, spin-allowed, electronic excitations of porphyrins and related compounds in supersonic expansions.³ In this Letter we report on the results of an experimental study of the $S_0 \rightarrow S_1$ transition (the Q band) and of the $S_0 \rightarrow S_2$ transition (the Soret, B band) of zinc tetrabenzoporphyrins (ZnTBP) in pulsed supersonic expansions of He, addressing the following issues.

(1) *Electronic Level Structure.* ZnTBP constitutes a symmetrically substituted metal porphine, characterized by a point group D_{4h} , whose $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are expected to be degenerate.⁴ The beautiful spectroscopic work on site-selection spectroscopy of metal porphyrins and metal tetrabenzoporphyrins in Shpolskii hosts^{5,6} demonstrated the lifting of the degeneracy by the crystal field. It will be interesting to obtain direct evidence for the degeneracy of the S_1 and S_2 states of the "isolated" metal tetrabenzoporphyrin molecule.

(2) *Vibrational Level Structure.* The elucidation of the vibrational excitations⁴ in the S_1 and S_2 states of ZnTBP is of interest for the characterization of the excited-state nuclear potential surfaces and for the elucidation of the effects of vibronic coupling and of Jahn-Teller instability.⁴⁻⁶

(3) *Electronic Relaxation from the S_1 State.* The lifetimes of photoselected vibrational excitations in the S_1 electronic manifold, interrogated by time-resolved spectroscopy, provide pertinent information regarding the mechanisms of intramolecular electronic-vibrational energy degradation and the effects of excess vibrational energy in the dynamics of electronic relaxation in a huge isolated molecule.⁷

(4) *Interstate Coupling and Radiationless Decay of the S_2 State.* The $S_2(B)$ state of metal porphyrins and of related compounds exhibits efficient interstate electronic relaxation, which occurs on the picosecond or the subpicosecond time scale.⁴ No quantitative information is currently available regarding the time scale of these ultrafast relaxation processes. The lifetimes of the S_2 state of ZnTBP appears to be relatively long, as indicated by the moderate line broadening ($\sim 6 \text{ cm}^{-1}$) of the Soret band in solid Ar,⁸ and by the relatively high ($\sim 10^{-3}$) $S_2 \rightarrow S_0$ emission quantum yield in solution, which imply a S_2 lifetime of $\sim 2 \text{ ps}$.⁸ The energy gap separating the electronic origins of the S_2 and S_1 states in ZnTBP is $\sim 9000 \text{ cm}^{-1}$,^{4,8} whereupon the S_2 - S_1 coupling in this huge molecule is large, being expected to correspond to the statistical limit.⁷ We shall provide spectroscopic information on the S_2 - S_1 "statistical type" interstate coupling in the ZnTBP molecule, which results in semiquantitative information concerning the time scale for electronic relaxation from the Soret band in this isolated large molecule.

Experimental Section

Laser spectroscopy of ZnTBP was conducted in seeded pulsed supersonic expansions of He. The utilization of pulsed jets allows for the use of modest pumping systems for the production of high-flow supersonic expansions and

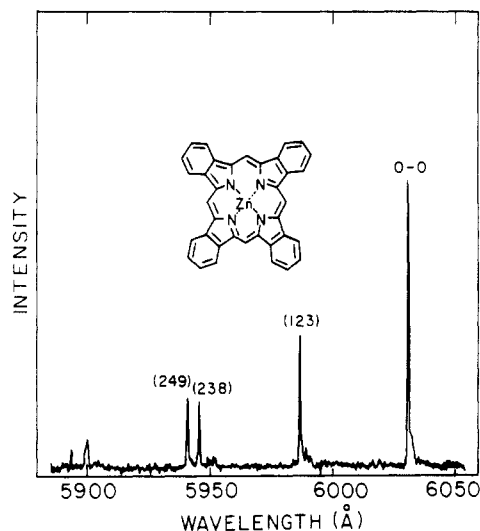


Figure 1. Fluorescence excitation spectrum in the region 5890–6050 Å of the ZnTBP molecule seeded in pulsed supersonic expansions of He. ZnTBP was heated in the nozzle chamber to 500 °C, seeded in He at $p = 1600$ torr, and expanded through a 0.06-cm nozzle. The exciting dye laser crossed the jet at 12 mm below the nozzle. Numbers in brackets represent the energies of vibrational excitations (in cm^{-1}) above the electronic origin (0–0).

drastically reduces material consumption. Porphyrin spectroscopy in jets requires the use of high-temperature (~ 350 °C for porphyrins,^{9,10} 420 °C for tetraphenylporphyrins,^{3,9} and ~ 500 °C for ZnTBP¹¹) supersonic nozzles. A pulsed supersonic jet source, which can be operated routinely in the temperature range 20–520 °C, was constructed.¹⁰ The gas pulse, which was interrogated by delayed laser-induced fluorescence (LIF) from a seeded jet, was characterized by a width (fwhm) of 200 μs . The nozzle diameter was 0.06 cm. The He gas at the stagnation pressures $p = 1500$ –2500 torr was sent through the nozzle containing the solid sample of ZnTBP (commercially obtained from Porphyrin Products, USA), which was heated to 500 °C. The vapor pressure of ZnTBP was $\sim 10^{-1}$ torr^{8,11} at 500 °C. The LIF spectra did not change by varying the nozzle temperature in the range 475–500 °C and did not show any evidence for thermal decomposition. The pumping system consisted of a 4-in. diffusion pump backed by a rotating pump with a pumping speed of 500 L min^{-1} . The terminal mach number, M , of the jets, estimated for typical working conditions at $p = 2000$ torr and $T = 773$ K, is $M \approx 100$. The seeded supersonic expansion was crossed by a dye laser (spectral width 0.3 cm^{-1} , pulse length 5 ns) at 10–15 mm down the nozzle. We have monitored (a) fluorescence excitation spectra and (b) time-resolved spectra.

(a) The fluorescence emitted in the range $\lambda > 5100$ Å was detected by a photomultiplier and recorded as previously described.¹² The LIF spectra are normalized to the laser intensity.

(b) The total fluorescence resulting from excitation at a fixed laser wavelength was focused on a photomultiplier, recorded by a biomation transient recorder, with a time resolution of 2 ns/channel, and averaged by a signal averager. The laser stray light monitored by this detection system was characterized by a nearly exponential decay

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with a decay time of 5.5 ns. Molecular decay lifetimes, τ , in the range $\tau = 1$ –15 ns were determined as the difference between the normalized first moment of the fluorescence signal and the normalized first moment of the laser pulse. This moment method is reproducible within ± 5 ns. Lifetimes determined by crossing the supersonic expansion with the laser at $x = 10$ mm ($x/D = 16$) and at $x = 15$ mm ($x/D = 25$) were found to be identical within the experimental uncertainty, so that collisional dumping effects are negligible.

Energetics of S_1

Figure 1 shows the fluorescence excitation spectrum in the range 5890–6050 Å of ZnTBP seeded in a supersonic expansion of He at $p = 1600$ torr. The spectrum is practically free from hot vibrational bands and from vibrational sequence bands. This LIF spectrum corresponds to the electronic vibrational excitations of the bare ZnTBP molecule rather than to He–ZnTBP complexes, as decreasing the downstream temperature by increasing the stagnation pressure of He from 1200 to 2400 torr did not affect the positions and the relative intensities of these spectral features. No additional spectral features were observed in the range 6050–7000 Å. Accordingly, the lowest-energy, intense, spectral feature at 6031.6 Å (16579 cm^{-1})¹³ is assigned to the electronic origin (0–0) of the $S_0 \rightarrow S_1$ transition. The spectral features corresponding to the 0–0 and to the lowest vibrational excitations of the $S_0 \rightarrow S_1$ transition of ZnTBP have widths (fwhm) of 1.5 – 3.0 cm^{-1} , presumably due to unresolved rotational structure. The energy range $E_v = 0$ – 400 cm^{-1} above the electronic origin of S_1 reveals three fundamental vibrational excitations at (a) 123 cm^{-1} , (b) 238 cm^{-1} , and (c) 249 cm^{-1} (Figure 1). These S_1 vibrational frequencies of the “isolated” molecule are close to the three lowest vibrational frequencies (131 , 242 , and 264 cm^{-1}) for the S_0 state of ZnTBP in *n*-octane.^{14,15}

Proceeding to higher energies in the range 5480–5895 Å, we were able to observe and analyze well-resolved vibrational excitations in the S_1 manifold for excess vibrational energies up to $E_v = 1666\text{ cm}^{-1}$. Our spectroscopic data just reveal high vibrational excitations in the S_1 manifold, while no evidence was obtained for “symmetry breaking” effects in the doubly degenerate S_1 (1E_u) state of the “isolated” ZnTBP molecule.

Electronic Relaxation from S_1

The decay lifetimes, τ , of the individual lowest electronic–vibrational excitations in the Q band of the “isolated” ZnTBP molecule were found to be $\tau = 2.0 \pm 0.5$ ns for the 0–0 origin, $\tau = 1.9 \pm 0.5$ ns for excitation (a), $\tau = 1.3 \pm 0.5$ ns for excitation (b), and $\tau = 1.4 \pm 0.5$ ns for excitation (c). The pure radiative lifetime, τ_r , of S_1 estimated from the integrated oscillator strength is $\tau_r \approx 17\text{ ns}$.⁸ Thus, for the lowest excitation in S_1 we estimate $\tau/\tau_r \approx 0.1$. The efficient nonradiative decay manifests the effect of heavy atom enhancement of intersystem crossing.⁴ Our experimental lifetimes for the “isolated” molecule are consistent with the solution quantum yield data of Gradyusko and Tsvirko,¹⁶ being somewhat lower than implied by the quantum yield data of Gouterman et al.⁸

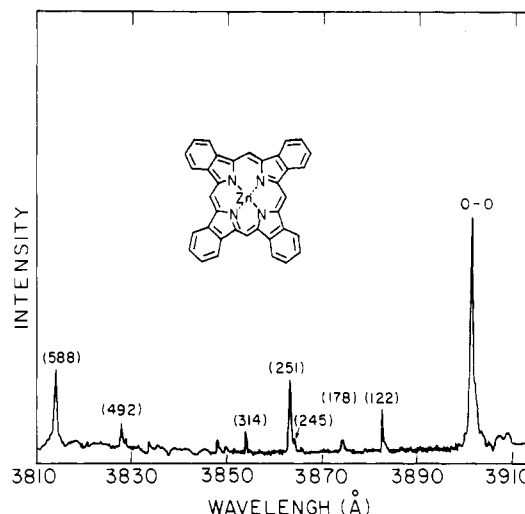


Figure 2. Fluorescence excitation spectrum in the region 3810–3910 Å of ZnTBP in pulsed supersonic expansions of He. Experimental conditions and marking of vibrational excitations as in Figure 1.

We have studied the dependence of the decay lifetimes of photoselected vibrational excitations in the S_1 manifold on the excess vibrational energy E_v . τ was found to be practically constant (within the large experimental uncertainty of $\pm 30\%$ up to $\pm 50\%$) on E_v up to $E_v = 1666\text{ cm}^{-1}$, where $\tau = 1.7 \pm 0.5\text{ ns}$. The independence of τ on the excess vibrational energy was observed recently also for moderately high vibrational excitations of some large molecules, i.e., tetracene¹² and pentacene,¹⁷ where above some threshold energy, \tilde{E}_v ($\tilde{E}_v = 1500\text{ cm}^{-1}$ for tetracene¹² and $\tilde{E}_v = 700\text{ cm}^{-1}$ for pentacene¹⁷) τ is independent of E_v . For ZnTBP it appears that $\tilde{E}_v = 0$. This universal feature of the invariance of τ with respect to E_v in the S_1 manifold of huge isolated molecules presumably reflects the manifestation of intrastate scrambling between vibrational levels (“vibrational energy redistribution”) on the interstate electronic relaxation process.¹²

The Soret Band

Figure 2 shows the fluorescence excitation spectrum of ZnTBP in the range 3810–3910 Å, which reveals the well-resolved electronic vibrational excitations of the Soret band. The electronic origin of the $S_0 \rightarrow S_2$ transition is located at 3901.5 Å (25631 cm^{-1}).¹³ Two low-lying prominent vibrational excitations in the Soret band (Figure 2) located at 122 and at 251 cm^{-1} are very close in their energies and relative intensities to the corresponding vibrations (a) 123 and (c) 249 cm^{-1} in the S_1 manifold. A similar correspondence prevails also for higher vibrational excitations in the two electronic manifolds, indicating that the potential energy surfaces are very similar in the S_1 and S_2 electronic states. It is interesting to note that the 245 cm^{-1} vibration in the S_2 manifold (Figure 2) is considerably weaker than the corresponding (b) 238 cm^{-1} vibration in S_1 (Figure 1), pointing toward the possibility that this vibration in the S_1 state is involved in vibronic coupling or in the Jahn–Teller coupling. Again, no experimental evidence was obtained for static “symmetry breaking” effects on the degenerate S_2 state of ZnTBP.

Relaxation from S_2

The spectroscopy of the Soret band provides information on interstate relaxation, which presumably involves S_2 – S_1 coupling and radiationless decay. A cursory examination of the electronic origins of the $S_0 \rightarrow S_1$ Q band and of the

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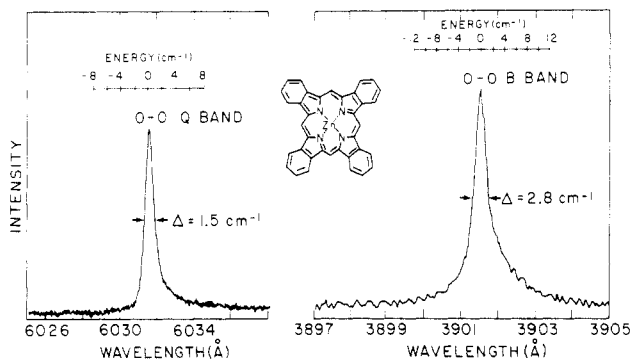


Figure 3. The electronic origins of the $S_0 \rightarrow S_1$ and of the $S_0 \rightarrow S_2$ transitions of ZnTBP in seeded supersonic expansions of He. Experimental conditions as in Figure 1.

$S_0 \rightarrow S_2$ Soret band, portrayed in Figure 3, indicates that the line width of the Soret band exhibits additional broadening. In view of the close similarity between the nuclear potential surfaces in the S_1 and S_2 states, we can infer that the rotational constants for these two electronic states are very similar, whereupon rotational broadening in the S_1 and S_2 origins is practically identical. Accordingly, we attribute the extra broadening in the Soret band to electronic relaxation of the S_2 state, which corresponds to the statistical limit.⁷ An estimate for the contribution δ to the line width of the S_2 origin, which is due to inter-state coupling, is obtained by subtracting from the width

(fwhm) of S_2 the rotational width (fwhm) of S_1 . From the data of Figure 3, we get $\delta = 1.3 \text{ cm}^{-1}$ as a crude estimate for the homogeneous relaxation broadening of the electronic origin of S_2 . Accordingly, the upper limit for the lifetime, $\tau(S_2)$, of this state is $\tau(S_2) > \hbar/\delta = 4 \text{ ps}$. This estimate of $\tau(S_2)$ in the isolated ZnTBP molecule is in excellent agreement with the lifetime $\tau(S_2) = 2.5 \text{ ps}$ reported by Gouterman et al.⁸ from solution quantum yield data. The modern theory of radiationless transitions⁷ implies that the rate of electronic relaxation of a single vibronic level of a large molecule, which corresponds to the statistical limit, is practically invariant to perturbations exerted by an "inert" medium. This theoretical result is not sufficient to rationalize the close correspondence between the lifetime of the electronic origin of S_2 in the "isolated", ultracold, ZnTBP molecule and the lifetime of the sequence-broadened S_2 origin in solution.⁸ We have to assert that the electronic relaxation rates of individual vibronic levels within the S_2 manifold, which are populated within the sequence congested solution band at room temperature, exhibit a weak dependence on the excess vibrational energy. This weak dependence of τ on E_v , indirectly inferred for the S_2 state, is analogous to the weak dependence of τ on E_v directly observed for the S_1 manifold.

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A Flowing Afterglow Source of $\text{Hg}(^3\text{P}_0)$ and $\text{Hg}(^3\text{P}_2)$ Atoms: Application to $\text{HgX}(\text{B})$, $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I , Formation Kinetics

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Passing a partially mercury saturated flow of Ar through a low power, hollow-cathode discharge gives $\text{Hg}(^3\text{P}_2)$ and $\text{Hg}(^3\text{P}_0)$ metastable atom concentrations of $\sim 5 \times 10^9 \text{ atoms cm}^{-3}$ in a flowing afterglow reactor. The reactions of $\text{Hg}(^3\text{P}_2)$ with molecular halogens have been studied by observation of the low-pressure, collision-free $\text{HgX}(\text{B})$, $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I , chemiluminescence. This appears to be the first report of the $\text{HgF}(\text{B-X})$ emission spectrum.

Introduction

Chemical and excitation transfer reactions with high branching fractions for formation of electronically excited state products are of importance for potential laser applications and for insight into the dynamics provided by the detailed product state distributions given by analysis of the spectra. Reactions yielding $\text{HgX}(\text{B})$, $\text{X} = \text{halogen}$, are of current interest because of the developmental effort in mercury halide lasers.^{1,2} The reactions of the triplet states of the $\text{Hg}(6s, 6p)$ multiplet previously have been

shown to yield $\text{HgX}(\text{B})$ with branching fractions highly dependent on the spin-orbit state.³⁻⁶ In the present study we have developed a flowing afterglow technique which produces the $\text{Hg}(^3\text{P}_2)$ and $\text{Hg}(^3\text{P}_0)$ states in Ar carrier gas. With this technique the reactions of these two states can be systematically investigated with ease. In this Letter we describe the flowing afterglow method and report the $\text{HgX}(\text{B-X})$ spectra from the reaction of $\text{Hg}(^3\text{P}_2)$ with F_2 , Cl_2 , Br_2 , and I_2 . Since the lifetimes of the $\text{HgX}(\text{B})$ states are $< 30 \text{ ns}$,⁷ $\text{HgX}(\text{B-X})$ spectra contain collision-free in-

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