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Gas-Phase Ion Thermometry: Internal Energy and Cooling Processes in Dioxane Ion Measured Using Competitive Photodissociation

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Abstract: From photodissociation at several known wavelengths in the ion cyclotron resonance ion trap, the ratio of m/z 57 to 58 photoproduct ions was calibrated as a function of the internal energy of dissociating parent 1,4-dioxane ions. This calibration was then used as an internal thermometer function to monitor the cooling of dioxane ions, initially prepared with an average of 0.34 eV of internal energy by electron impact ionization. The rate constant for collisionless (IR-radiative) cooling of the ions was found to be 1.0 s^{-1}. Bimolecular collisional cooling rate constants were found to be 9×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for Ar quench gas (0.016 times the orbiting collision rate) and 4.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for SF_6 quench gas (0.06 times the orbiting collision rate).

A challenge in studying the chemistry of isolated gas-phase molecules is the determination of the internal energy of the molecule at the time of the chemical event being studied. Recent interest in the behavior of gas-phase ions under collision-free or limited-collision conditions has made this a particularly pressing problem. The approach described here, based on competitive photodissociation, gives particularly straightforward and convincing internal-energy measurements.

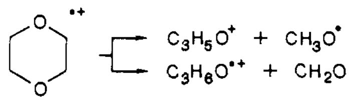
Under collision-free conditions, vibrationally hot ions cool by infrared fluorescence. The infrared radiative cooling of isolated molecules in the temperature regime of a few hundred degrees kelvin is interesting, for example, in the modeling of interstellar chemical kinetics,[1] but because this is such a slow process, few laboratory measurements have been possible. The ability to examine such processes, and to observe the transition to collisional cooling as the pressure is raised, is an outstanding capability of trapped-ion experiments.[2-7]

Polyatomic molecules of more than a few atoms prepared with a given amount of internal energy rapidly reach statistical equilibrium among the internal degrees of freedom, and the resulting statistics are so close to those of a canonical ensemble that it is useful to assign an internal temperature. However, direct measurement of this temperature is usually not easy. When feasible, spectroscopic methods such as observation of hot-band intensities are useful,[8] but spectroscopic study of gas-phase ions is not yet widely practicable. Usually determination of the internal energy is more feasible, from which the internal temperature may be calculated. The ion vibrational temperatures discussed here were calculated from the internal energy assuming harmonic normal modes. A recent discussion[9] describes the significance and the calculation of the internal temperature of an isolated molecule using the temperature–energy relations of the canonical ensemble. The temperature of the internal degrees of freedom in a collision-free molecule is decoupled from, and unrelated to, the rotational and translational temperatures of the ensemble (which may not be well defined in any case).

Defining and thinking in terms of the internal temperature of an isolated polyatomic molecule has advantages of clarifying and simplifying the understanding of various aspects of molecular behavior, and its relation to corresponding thermally equilibrated systems, even though the internal energy content of an isolated molecule is conceptually more straightforward than its internal temperature. For instance, working in terms of the internal temperature makes very simple the assignment of excitation probabilities for the individual normal modes of the molecule,[9] which is otherwise an elaborate and unintuitive statistical-mechanical exercise. Similarly, the radiative ion-relaxation kinetics coming from studies like those reported here can be connected immediately, through the unifying concept of internal temperature, to radiative relaxation and equilibration behavior of molecules in collisionally thermalized environments such as dense interstellar clouds. Such rich possibilities of simplification and interconnection motivate us to speak of the present results in terms of internal temperatures of the dioxane ions, even though this concept is not actually central to the methods and conclusions of this particular study.

For ions, it is particularly convenient to measure the internal energy by observing fragmentation processes, which are highly energy sensitive in at least two useful ways. First, the rate of fragmentation depends strongly on internal energy, and techniques such as time-resolved dissociative photoionization[10] and time-resolved photodissociation[3] have been successfully calibrated and used in this way. Second, when two fragmentation products are formed in competition, their ratio is often delicately energy sensitive.[11] The calibration and application of such an energy-dependent competition in dioxane ion is described here.

Dioxane ion fragments competitively into two products at m/z 57 and 58:



(1)

This system has been studied by energy-resolved techniques several times, although none of these prior studies was free of problems. Fraser-Monteiro et al.[10] measured the wavelength dependence of the fragment-ion photoionization yields (photoionization efficiency, or PIE, curves). Under various assumptions which may or may not be valid, these data can be converted to an energy dependence

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of the fragmentation pattern by taking the derivative of the PIE curves with respect to energy. A curve for the 57/58 ratio as a function of internal energy was derived in this way.[12]

Two photodissociation studies have also measured the energy dependence of this ratio. An ion-beam photodissociation study by Bowers' group yielded a curve in good agreement with the PIE-derivative curve, but it was not known with confidence whether the ions emerging from the ion source were thermalized, so that these results were not considered definitive.[12]

Our group performed an ICR (ion cyclotron resonance) ion trap photodissociation study which yielded a 57/58 ratio curve lying significantly above these others.[12] It was considered likely that the ions in this study were not thermalized, and the assumption of 0.3 eV of excess internal energy in the electron-impact-produced ions reconciled the ICR study with the other results. The present ICR photodissociation study using more advanced techniques confirms that excess internal energy did indeed shift the previous ICR measurements.

Experimental Section

Most of this work was carried out on the homebuilt ICR spectrometer with phase-sensitive detection which has been described in previous trapped-ion photodissociation studies.[11,13] Some of the measurements were repeated using an instrument of similar physical characteristics equipped with an IonSpec Fourier-transform data sytem.

1,4-Dioxane from Aldrich (Spectrophotometric grade) or Fisher was used without further purification beyond several freeze–pump–thaw cycles. The dioxane pressure (0.5–1 $\times 10^{-8}$ Torr) and the collision gas pressures were measured by ionization gauge with standard corrections.[14]

Molecular ions of 1,4-dioxane were formed by electron impact at (nominally) 12.4 eV, which is about 3 eV above the ionization energy.[10] They were trapped with a trapping voltage of 3.7 V and a magnetic field of 1.4 T. Following the thermalization period, they were irradiated with a 50–100-ms pulse of light from the argon-ion laser, after which the photoproduct ion abundances were determined by the usual ICR detection sequence.

The laser ran at a power of 1–3 W with a ~1-cm beam size, giving a power of ~2 W cm^{-2} or a fluence of ~0.2 J cm^{-2}. Usually 25–40% dissociation of the parent ions were observed under these conditions. The laser pulse length was chosen to give ample dissociation while still being short compared with the characteristic times of the relaxation processes studied.

Vibrational temperatures were calculated via the standard statistical-mechanical relation for the average harmonic-oscillator energy in a canonical ensemble at a given temperature. In assigning the average internal energy of 0.10 eV to the thermalized dioxane ions, the assumption is that after a long enough period of radiative equilibration with the cell walls and collisional equilibration with the neutral dioxane vapor, the ion population will come to thermal equilibrium at the cell temperature of 350 K, and that the average internal energy of an ion will then be the sum of the average energies of all its vibrational modes. The vibrational frequencies of dioxane ion were assumed to be as given in ref 10.

Results and Discussion

The lowest energy fragmentations of dioxane ion (to give *m/z* 44 and 45) require 1.20 and 1.27 eV of energy, respectively,[10] but at the photon energies used here little *m/z* 44 or 45 was formed, and only the *m/z* 57 and 58 products were abundant. Their formation thresholds (from photoionization) are 2.0 and 1.4 eV, respectively.[10] The photon energies used were between 2.41 and 2.71 eV; in this range the 57/58 ratio was found to be between 1 and 5.

It will be useful to define the quantity E_x, the excess ion internal energy, which is the ion internal energy in excess of the thermal internal energy at the cell temperature. The ion thermometric technique described here is accurately calibrated for measuring E_x, presuming the cell temperature to be the same during all measurements. The cell temperature is not precisely known, and moreover the thermal ions have a somewhat broad distribution of internal energies, so that the E_x measurement can only be converted into total ion internal energy in an approximate way.

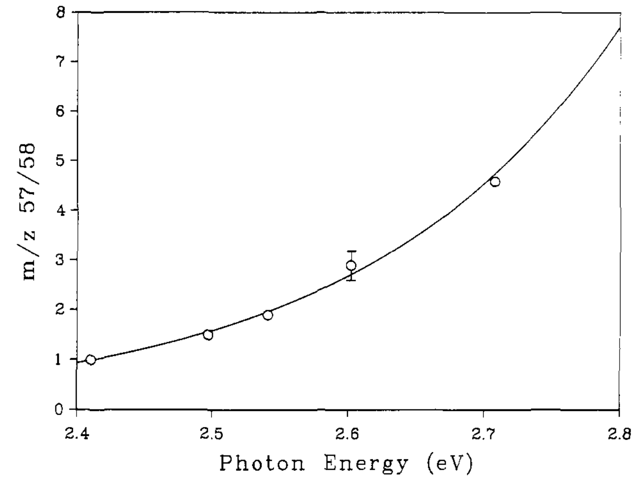
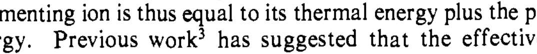


Figure 1. Ratio of *m/z* 57 and 58 photoproducts as a function of photon energy for 1,4-dioxane parent ions photodissociated after extensive thermalization. The solid smooth curve has no significance other than to guide the eye.

It seems at first sight as if the results of this study would be highly sensitive to the value (0.10 eV) assigned to the average internal energy of thermalized dioxane ions. The advantage of using the variable E_x is that the important results (namely the cooling curves, relaxation rates, and nascent-ion energy) are actually independent of the assigned thermal energy: Only the thermometric curve, Figure 2, giving absolute energies versus 57/58 ratios, changes if the assumed cell temperature is changed from the value of 350 K used here.

This work consisted of two principal parts. First the 57/58 ratio was calibrated as a function of ion internal energy E_x by photodissociation of thoroughly thermalized parent ions at several wavelengths. Then, the calibration curve having been established, competitive photodissociation was applied as the thermometric technique to characterize the cooling of initially excited dioxane ions, both by infrared radiative cooling at low pressure, and by collisional cooling with two different bath gases. The sequence of events is summarized in eq 2.



(2)

Thermometric Curve. Figure 1 shows the 57/58 ratio for photodissociation of the dioxane parent ion at five argon-ion-laser wavelengths. After electron impact the parent ions were thermalized during a 1-s thermalization period at 3.2 $\times 10^{-6}$ Torr of SF_6, a period which allows about 100 ion-neutral collisions as well as substantial radiative ion cooling. Based on the results of the next section, these conditions are adequate for good equilibration of the ions to ambient temperature. The internal energy of each fragmenting ion is thus equal to its thermal energy plus the photon energy. Previous work[3] has suggested that the effective cell temperature is around 350 K, although because of local heating by the filament the cell temperature is nonuniform. Taking 350 K as an approximate value, we may assign an average thermal vibrational energy of 0.10 eV.

The 57/58 ratio increases smoothly with increasing ion internal energy. Adding the average thermal energy of 0.10 eV, the curve of Figure 1 can be converted to a plot of 57/58 ratio versus total ion internal energy, as is shown in Figure 2. These results are in good agreement with the curve adopted as the best estimate in ref 12. Since the previous results were not considered very reliable, the present results can be taken as the best available thermometric calibration for this competitive fragmentation. As noted above, the absolute energy axis of Figure 2 is uncertain to the extent that the cell temperature, and thus the correction for ion thermal energy, is not well known. Assuming that the cell

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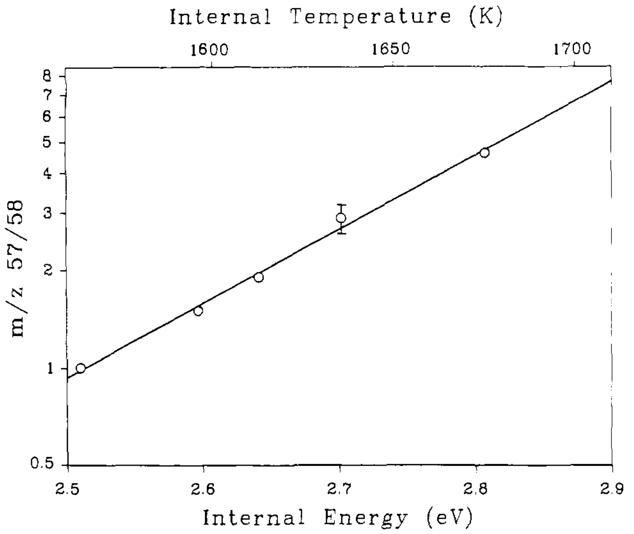

Figure 2. Calibration curve established for *m/z* 57 to 58 ratio as a function of the total internal energy (and internal temperature) of the fragmenting dioxane ion (obtained from the results of Figure 1 by adding 0.10 eV of average thermal energy to the photon energy). The solid line is from eq 3.

temperature is uncertain to perhaps ±30 K, the absolute energy axis of Figure 2 is uncertain to about ±0.03 eV.

The 57/58 ratio is found empirically to fit the relation

$$\ln (R) = -13.24 + 5.27E_t \tag{3}$$

where R is the 57/58 ratio, and E_t is the total internal enegy (assuming 0.10 eV thermal energy) of the ions in eV, over the energy range 2.52 to 2.82 eV.

Cooling of Hot Ions. The parent ions formed by electron-impact ionization initially have several tenths of an eV of superthermal internal energy, and the thermometric capability developed above offers the means to observe the relaxation of these hot ions toward ambient temperature.

Collisionless Cooling. Under collision-free conditions, cooling is via infrared radiation. Since this is expected to have a time scale of hundreds of milliseconds or seconds in this temeprature regime,[13] the pressure (or at least the partial pressure of efficient quench gases) should be less than 1×10^{-8} Torr in order for collisions not to contribute significantly to the cooling. While a comprehensive study of collisional quenching by parent dioxane was not carried out, comparison of cooling curves at 0.9×10^{-8} and 5×10^{-8} Torr indicated a collisional cooling rate constant of about 5×10^{-10} cm^3 molecule^{-1} s^{-1} (about half the orbiting collision rate). Under the low-pressure conditions used in the radiative cooling studies, collisional relaxation was thus expected to contribute about 20% to the overall relaxation; this collisional contribution was subtracted to obtain the radiative cooling rate.

Figure 3 shows the cooling behavior of the parent ions at a parent pressure of about 0.9×10^{-8} Torr. The excess internal energy E_x is shown as a function of time following the electron beam pulse. The relaxation closely follows first-order cooling kinetics (linear plot of ln (E_x) versus time) with a cooling rate constant of 1.2 s^{-1}, which indicates a collisionless cooling rate constant of 1.0 s^{-1}. In view of this very long relaxation time, it is not surprising that the previous low-pressure ICR photodissociation experiments[12] were affected by unrelaxed excess internal energy.

For one other ion, chlorobenzene parent ion, a collisionless relaxation rate has been measured in the region within a few tenths of an eV of room temperature.[3] Its low-pressure cooling rate constant of 0.4 s^{-1} is even slower than that found here for dioxane ion.

Extrapolation of the curve of Figure 3 back to zero time agrees well with similar extrapolations of the higher pressure curves discussed below, and indicates an excess internal energy of about 0.34 eV for nascent dioxane ions after electron-impact ionization. This seems entirely reasonable for low-energy electron impact. For comparison, if ionization produced a completely flat distribution of parent ion internal energies, the average parent ion energy would be about 0.6 eV, since parent ions undergo fragmentation at internal energies above 1.2 eV. The present measurement showing an average nascent internal energy somewhat less than this is consistent with the known discrimination of electron impact ionization in favor of lower threshold processes corresponding to lower internal energies of the ion.

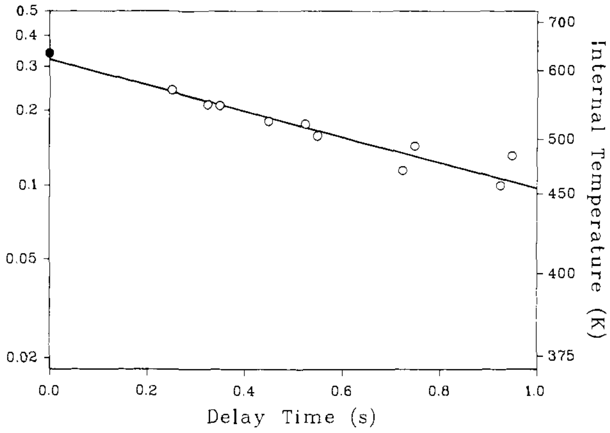

Figure 3. Collisionless relaxation of initially excited dioxane ions, obtained by measuring the 57/58 ratio from 515-nm photodissociation at various times after the electron beam pulse. The solid circle represents the consensus value of the initial electron-impact energy deposition of 0.34 eV obtained from all the data. The excess internal energy values (E_x) plotted on the *y* axis are obtained directly from the measured 57/58 ratios by applying the calibration curve of Figure 2, subtracting the photon energy of 2.41 eV, and subtracting 0.10 eV of thermal energy, to give E_x.

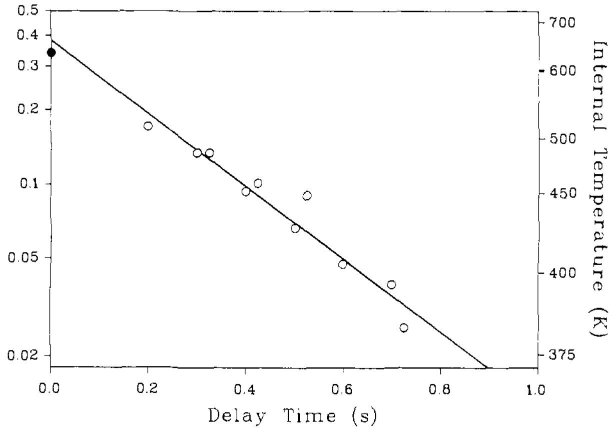

Figure 4. Collisional relaxation of dioxane ions by SF_6 collisions at an SF_6 pressure of 1.6×10^{-6} Torr. The E_x values were derived from the observed 57/58 ratios at 515 nm as described in the caption to Figure 3.

Collisional Quenching. Collisional cooling of the hot dioxane parent ions was studied for two quench gases, Ar and SF_6. For example, a cooling curve is shown in Figure 4 at an SF_6 pressure of 1.6×10^{-6} Torr. As was found in all cases, the cooling curve gives an excellent fit to first-order cooling kinetics (linear plot of ln (E_x) versus time). Such curves were taken at several pressures, and the collisional cooling rate constant was determined as the slope of the plot of cooling rate constant versus neutral concentration, as shown in Figure 5.

Note that two types of rate constant are used here. If the internal energy of the ion decreases exponentially with time (regardless of the mechanism of relaxation), we define the cooling rate constant k_1 as the apparent first-order rate constant for this cooling process (units of s^{-1}). For collisional cooling, this apparent first-order rate constant should be proportional to pressure, and we define the bimolecular collisional cooling rate constant k_p as

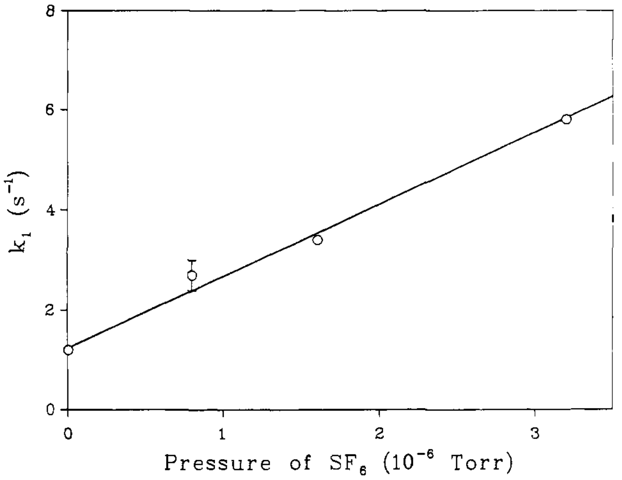

Figure 5. Collisional cooling rate constants k_1 as a function of SF_6 pressure. Each point is derived from the slope of a plot like that of Figure 4.

the derivative of the first-order cooling rate constant with respect to pressure (units of cm^3 molecule^{-1} s^{-1}. Then the overall relaxation rate constant k_1 is expressed as

$$k_1 = k_r + k_p P \tag{4}$$

where k_r is the radiative cooling rate constant, and P is the pressure of neutrals.

The resulting bimolecular rate constants for cooling of hot ions were 9×10^{-12} cm^3 molecule^{-1} s^{-1} for Ar and 4.5×10^{-11} cm^3 molecule^{-1} s^{-1} for SF_6. For Ar, the cooling rate constant is 0.016 times the calculated orbiting rate constant, while for SF_6 the ratio is 0.06. Thus it requires 50 collisions for Ar to remove half the excess internal energy, while this requires 12 collisions for SF_6.

For both of these neutrals, the collisional efficiency of cooling is low, but it is in line with observations of cooling of other similar-sized ions by these same two neutrals. It was found that it requires 77 argon collisions to cool bromobenzene ion from 2.5 to 0.25 eV excess energy,[15] which corresponds to a bimolecular cooling rate constant of 1.6×10^{-11} cm^3 molecule^{-1} s^{-1}; and it requires 5 collisions for SF_6 to cool benzene ion from 2.8 to 1.5 eV, a bimolecular cooling rate constant of 8×10^{-11} cm^3 molecule^{-1} s^{-1}.[16] The present results are thus quite comparable to the situation found for bromobenzene and benzene ion quenching.

Conclusions

The competitive-dissociation ion thermometry technique described here provides a convenient way of probing the internal energy of the ions at a chosen moment in time and in a region of space defined by the laser beam. Various diagnostic applications can be imagined in the study of physical and chemical processes involving heating or cooling of ions. Examples might be the study of energy deposition in charge-transfer ionization or multiphoton ionization of dioxane, or the study of collisional heating of dioxane ions by energetic ion-neutral collisions.

The ion for which competitive dissociation has been most thoroughly calibrated as a function of internal energy is *n*-butylbenzene ion, and this system is often considered as a standard test case for assessing ion excitation in mass spectrometers.[11] The competition to form $C_7H_7^+$ and $C_7H_8^+$ product ions has been measured as a function of parent ion internal energy for ions of well-characterized energy by charge-transfer ionization, by ICR photodissociation, and by photoelectron–photoion coincidence. For photodissociation work in the visible wavelength region dioxane ion is more convenient, because the m/z 57/58 ratio which serves the thermometric function is near unity, whereas for *n*-butylbenzene the m/z 91/92 ratio is closer to 0.1. The calibration for dioxane ion given here in Figure 2 is believed to be as precise and reliable as that for *n*-butylbenzene ion.

The collisionless cooling of dioxane ion in this energy regime, with a time constant of 1.0 s, is one of the slowest processes involving isolated ions which has been observed in the laboratory. Consideration of the slow radiative equilibration of an isolated ion with the environment is relevant to understanding deep-space chemistry of polyatomic molecules, and is increasingly important in mass spectrometry as the use of ion-trapping instruments increases.

The collisional cooling of dioxane ion by Ar and SF_6 affords no surprises, proceeding with collisional efficiencies typical for such systems. In the case of SF_6, collisional cooling is much slower than predicted by a full-equilibration model (in which the internal energy is statistically equilibrated between ion and neutral on each collision). Again, this is similar to what is observed in other comparable systems.[15] For argon quenching, the full-equilibration model is harder to specify, but the very inefficient quenching observed here is certainly slower than a full-equilibration prediction based on statistical partitioning into the argon translational degrees of freedom.

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Optical Properties of Metalloporphyrin Excited States

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Abstract: The absorption features of ${}^1(\pi,\pi^*)$, ${}^3(\pi,\pi^*)$, ${}^3(d,\pi^*)$, and (d,d) excited states of metalloporphyrins have been closely examined between 420 and 900 nm with subpicosecond/picosecond transient absorption spectroscopy. The spectra of all of these excited states exhibit strong but not readily distinguishable absorption between the Soret- and Q-band bleachings, a region used extensively and often exclusively in transient absorption studies on porphyrins. The absorption features between 600 and 900 nm are smaller than those observed in the Soret region but have distinctive characteristics that aid in assessing the presence or absence of a particular type of transient state. We discuss the electronic origins of the prominent bands in the excited-state spectra. Our results and discussion provide fundamental information on the optical properties of metalloporphyrin excited states and a much needed framework for better interpreting the results of in vivo and in vitro transient absorption studies on these complexes.

Transient absorption spectroscopy has played a central role in furthering the understanding of the primary charge-separation process in bacterial photosynthetic reaction centers,[1] the photoinduced release/rebinding of diatomic ligands from hemoglobin

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