Accurate Photothermal Calorimetry Using Cylindrical-Cell Thermal Lens Photometry

A. Chartier and S.E. Bialkowski
Department of Chemistry and Biochemistry
Utah State University
Logan, UT 84322-0300 USA

Photothermal spectrophotometry has been used to obtain calorimetric data on a variety of photo-initiated chemical systems for many years. Measurement of temperature change through the photothermal effect has been used to determine intermediate state enthalpies, excited triplet state enthalpies, and quantum yields. Recent experiments have brought into question the accuracy of these measurements since, in addition to the photothermal effect, several processes may result in refractive index changes thereby producing a response measured by photothermal spectrophotometry. Refractive index and specific volume changes may result from excited or intermediate state population changes. These produce photo-induced signals in addition to the temperature change. Auxiliary experiments requiring repeated measurements over a range of temperatures and/or solvent compositions must be performed in order to elucidate these effects.

This paper describes a means whereby the calorimetric data, i.e., that resulting from sample heat or enthalpy, can be determined directly and without regard for population dependent index and specific volume changes. The apparatus is based on optical excitation of samples contained in a cylindrical cell. Samples are illuminated with a spatially isotropic, constant irradiance or integrated irradiance source. A probe laser is used to monitor the photothermal lens element formed in the sample cell. The lens thus formed is due to thermal diffusion of excess heat through the cell walls, not to a spatially anisotropic excitation source as is in photothermal spectrophotometry of homogeneous samples using laser irradiation. Since thermal diffusion is the only mechanism for creating a refractive index gradient, effects such as volume and index changes due to excited states do not result in measurable signals. The theory for thermal lens formation is presented. Data obtained on charge transfer pairs known to produce large specific volume changes in aqueous solution are used to illustrate the effectiveness of the technique. Experiments performed in a variety of solvents and at different temperatures are used to illustrate flexibility and the ease at which calorimetric data can be obtained.