Thermal Equilibration During Cavitation

Flint and Suslick (1) reported the observation of $C_2(d^3\Pi_g - a^3\Pi_u)$ Swan emission from the ultrasonic cavitation of silicone oil and other hydrocarbons. The observed emission spectrum was accurately simulated by a rotational and vibrational distribution near 5000 K. We wish to emphasize here caveats against the assumption that this effective temperature of excited state C_2 necessarily represents the temperature of other gases in the cavitation event. Indeed, no single temperature describes all species present in a cavitation event. During the collapse of a cavitation bubble, the local conditions are extraordinarily dynamic, both spatially and temporally. The thermal spike created during acoustic cavitation means that the effective temperature in different regions of the bubble and surrounding liquid varies tremendously. The measurement of the Swan band emission temperature represents only the effective temperature of C_2 in the $d^3\Pi_g$ excited state.

The product molecules of a chemiluminescent reaction contain the excess energy of the chemical reaction that formed them, in addition to the initial thermal energy of the reactants. The initial distribution of states will collisionally relax toward a thermal distribution; these collisions, however, can also remove molecules from the electronic excited state necessary for emission. When the collisional rate is sufficiently rapid (that is, when the pressure is sufficiently high), the intensity of emission will be pressure dependent, but the observed vibrational and rotational state distribution will be independent of pressure. The population distribution of the emitting species will depend only on the initial product distribution and on the ratio of the rates of energy redistribution to the rate for quenching of the excited electronic state.

In flames and plasmas, this can give an effective emission temperature for excited state C_2 well above that of the surrounding gas. For example, C_2 Swan emission in oxygen-acetylene flames is observed with a rotational distribution of 7000 to 5000 K (depending on the pressure), while the adiabatic flame temperature limit is 3300 K (2). High resolution spectra show that the distribution is not quite Boltzmann, with high rotational levels described by a higher temperature than low rotation levels. Swan band emission is also observed

from the gas effluent of dc-arc-jet plasma deposition of diamond films; the emission envelope is fit to a rotational and vibrational temperature of 5000 K (3, 4). In the same jet, the rotational distribution of the ground state C₂ and CH were both measured by laser-induced fluorescence and found to be well described by a temperature of 2100 K (4). The excited-state radicals are removed by both chemical reaction and energy transfer collisions, whereas the ground-state radicals are removed only by chemical reaction; thus the ground state radicals have a longer lifetime in which to become equilibrated with the bulk gas temperature.

There are, of course, important differences between these systems and a cavitating bubble. For any given spatial position for flames and plasma jets, a steady state temperature for the gas may be achieved. In contrast, the dynamic nature of the cavitation event is inherently more complicated, and its characterization must include a coupled temporal and spatial description. In addition, flames and plasmas consist of gases that are generally below 1 bar, whereas cavitation will occur, at least transiently, in a supercritical fluid with peak pressures of perhaps 1 kbar. The extrapolation of quenching rates measured in moderate pressure flames to the conditions of a cavitating bubble could be problematic if nonlinear mechanisms in the supercritical fluid (such as cage effects) alter the chemiluminescent product distribution product distribution or the ratio of quenching versus energy redistribution rates.

During the cavitation event, the excited state C₂ emission may not be fully equilibrated with other species in the cavitating bubble. This problem of equilibration, which was briefly discussed in (1), is emphasized here. The cavitation event may not allow thermal equilibration either between the emitting species and other gas molecules or among the rotational, vibrational, and translational manifolds of the emitting species itself. Different electronic states of the same molecule may even have different effective temperatures (4). During cavitation, there is an apparent equilibration of rotational and vibrational temperatures within $d^3\Pi_g$ C₂ molecules. As reported in (1), a single effective temperature does provide a good description of the population distribution of both the rotational and vibrational excited states of $d^3\Pi_g C_2$ formed during cavitation. This is not true for all sonoluminescence; as noted, CN* emission is not well represented by a single temperature (1). The initial product state distribution of CN* is nonthermal and does not equilibrate within its lifetime.

An alternative measure of an effective temperature of cavitation can be provided by the use of chemical kinetics as an in situ thermometer. Such comparative rate thermometry has been used to measure an effective reaction temperature for sonochemical reactions produced by cavitation (5). This analysis used relative rate determinations of CO dissociation from metal carbonyls, which is completely independent of C_2 formation, excited state lifetimes, or sonoluminescence. There is excellent agreement between the effective temperature of excited state C_2 (5080 ± 160 K) and the reaction temperature determined by comparative rate thermometry $(5200 \pm 500 \text{ K})$ (5).

The spatial and temporal temperature profile of a cavitating bubble remains an important question that is not yet resolved. The application of time-resolved measurements of a single cavitating bubble may help provide a full profile of the cavitation event.

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