

Sonoluminescence from non-aqueous liquids

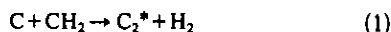
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Our understanding of the chemical effects of high-intensity ultrasonic irradiation of liquids is still quite limited. It is generally accepted that sonochemistry results from acoustic cavitation: the creation, growth, and implosive collapse of bubbles in ultrasonically irradiated liquids¹. The mechanism of sonoluminescence in aqueous systems has been a matter of some dispute; recent discussions have suggested at least three possible origins: black-body emission², chemiluminescence from radical recombination³, and electric discharge⁴. Few studies of non-aqueous sonoluminescence, however, have been conducted⁵⁻⁷. We present here the first spectrally resolved sonoluminescence spectra from hydrocarbon • r.d halocarbon liquids. These spectra originate unambiguously from excited-state molecules created during acoustic cavitation. These high-energy species probably result from the recombination of radical and atomic species generated during the high temperatures and pressures of cavitation.

The sonoluminescence spectrum of dodecane originates from excited state C₂, specifically from the d³Π_g → a³Π_u transition—the so-called Swan band (Fig. 1). The four bands at 435, 465, 510 and 550 nm correspond to Δv = +2, +1, 0, and -1 of the vibrational manifold, respectively. The sonoluminescence spectra of mesitylene, 4-heptanone and n-butylcyanide are qualitatively similar to that of dodecane, but with lower intensities and slight changes in the relative intensities of the vibrational bands.

Swan band chemiluminescence is seen from hydrocarbons in a wide variety of conditions, including flames⁸, shock tubes^{9,10}, shock pyrolysis¹¹, plasmas¹², laser ablation¹³, and low pressure discharges¹⁴. Grebe and Homann¹⁴ in their study of the gas-phase reactions of acetylene with oxygen and hydrogen atoms (C₂H₂/O/H) in a low-pressure discharge flow reactor, provided compelling evidence that one reaction responsible for the generation of C₂(d³Π_g) was



For several reasons, this is also a plausible step in the sonochemical formation of C₂(d³Π_g). First, the pressures and temperatures achieved during acoustic cavitation are similar to those reached in shock tubes and plasmas. The effective temperature reached during cavitation in alkane solvents was recently determined¹⁵ to be 5,200 K in the gas phase and ≈ 1,900 K in the liquid region surrounding the collapsed bubble, when the total vapour pressure is 5 torr. Since the efficacy of cavitation collapse is inversely dependent on the total vapour pressure¹⁶ the effective temperatures generated in these sonoluminescent systems (whose vapour pressures are much less than 5 torr) must be even higher. Second, carbon-carbon bond cleavage of alkanes and the formation of radicals from non-aqueous liquids during ultrasonic irradiation has been documented¹⁷. The sonolysis of even n-alkanes generates a wide variety of homolytic products via a radical chain pathway. Atomic carbon and CH₂ can be created through such mechanisms. Indeed, the final products observed¹⁸ from alkane sonolysis include large amounts of H₂, CH₄ and C₂H₂, consistent with the observed sonoluminescence. Third, other techniques which generate comparable temperatures and pressures on a macroscopic scale also produce Swan band emission. For example, the shock tube pyrolyses of benzene⁹ and acetylene¹⁶ produced chemiluminescence spectra that could be assigned to C₂(d³Π_g), and when liquid benzene was shock compressed to between 24 to 63 GPa, emission from the Swan bands of C₂ was also observed¹⁹.

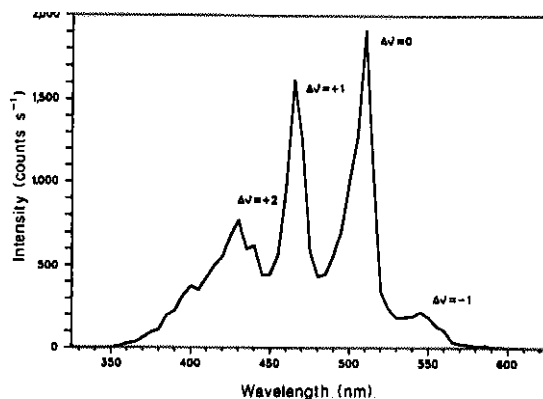


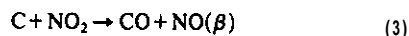
Fig. 1 The sonoluminescence spectrum of dodecane under argon. Emission is from excited state C₂ (d³Π_g → a³Π_u). The cell temperature was -4°C; vapour pressure at this temperature²⁵ is 0.006 torr.

Methods. All chemicals and gases were purified by standard methods²⁶. The irradiation cell has been described in detail elsewhere²⁷; the source of ultrasound was a direct immersion titanium horn operating at 20 kHz, which produced a 1 cm diameter collimated beam (far field region) with intensity of ≈ 25 W cm⁻² at the horn surface. Solutions were sparged with Ar during irradiation. Emitted light was collimated, passed into 0.25 m monochromator with 2.0 cm slits, and detected with a RCA 1P28 photomultiplier tube connected to a boxcar integrator. Spectra were collected at 5 nm increments and were not corrected for detector response.

The sonoluminescence spectrum of tetrachloroethylene is shown in Fig. 2. This can also be assigned to the C₂ (d³Π_g → a³Π_u) Swan transition. The change in the relative vibrational band intensities and the strong diminution of the Δv = +2 band indicates a lower internal energy in C₂* for tetrachloroethylene than for dodecane. This is consistent with the decrease in cavitation heating observed with increased total vapour pressure¹⁶. Several systems involving organic halides produce C₂* chemiluminescence, including reactions with hydrogen atoms at low pressure²⁸, with sodium atoms in a heat-pipe-oven reactor¹⁸, and with N₂O and sodium²⁹. The formation of C₂* is attributed to the reaction shown in equation 2. The abstraction of a halogen atom by another atom (H or Na) generates the species that eventually luminesce. During ultrasonic irradiation, however, these radicals are formed by the high temperatures of the cavitation event. The sonochemistry of haloalkanes is little explored, although the sonolysis of chloroform to produce radicals and carbenes has been recently reported^{30,31}.



Figure 3 shows the sonoluminescence spectrum and the ultraviolet-visible absorption spectrum of nitroethane. The intense absorption of nitromethane at wavelengths below 375 nm prevents detection of any spectral features in the ultraviolet. This sonoluminescence emission can be assigned to the NO emission bands from the B²Π → X²Π transition (the so-called β bands), with Δv ≥ 12. The spectrum is not consistent with the chemiluminescence observed²³ from NO₂, which is a broad emission from 400 to 1,200 nm with a maximum at about 650 nm. The reaction of carbon atoms with NO₂ (equation 3) has been studied in a low-pressure gas discharge reactor²⁴, and was identified as the only plausible mechanism for the formation of NO(β). This mechanism is consistent with those proposed for C₂* sonoluminescence.



These sonoluminescence spectra of non-aqueous liquids demonstrate that ultrasound is a powerful chemical initiator and that significant chemistry occurs during ultrasonic irradiation even in the absence of reactive solutes. The similarity between

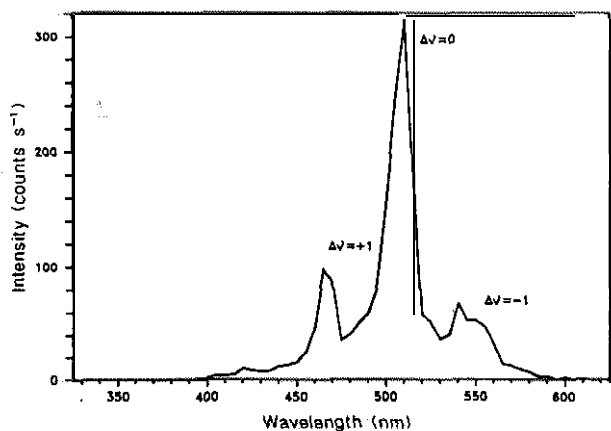


Fig. 2 The sonoluminescence spectrum of tetrachloroethylene under argon. Emission is from excited state C_2 ($d^2\Pi_g \rightarrow a^2\Pi_u$). The cell temperature was -16°C ; vapour pressure at this temperature²⁵ is 1.3 torr.

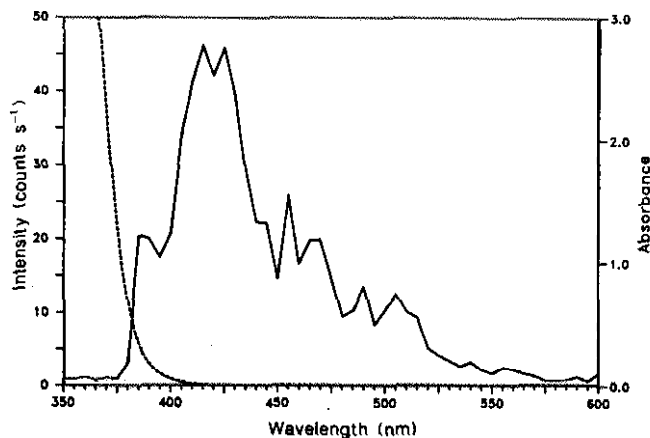


Fig. 3 The sonoluminescence spectrum of nitroethane under argon, scale at left. —, Emission from excited state NO ($B^2\Pi \rightarrow X^2\Pi$). The cell temperature was -19°C ; vapour pressure at this temperature²⁵ is 1.1 torr. - - - -, The ultraviolet-visible spectrum of nitroethane, 1 cm path length, absorbance scale at right.

sonoluminescence and the chemiluminescence seen with other high energy techniques (such as flames, plasmas, and shock tubes) indicates that similar chemistry is occurring during the ultrasonic irradiation of liquids.

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