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GAS-PHASE SPECTROPHONE MEASUREMENTS

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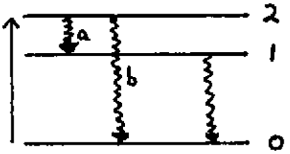
The resurrection of optoacoustic measurements on gases around 1960 did not depend significantly on the simple gas analysers which were being used at that time, but rather on the drive to find new techniques to study the details of vibrational-translational energy transfer. From the outset, then, the emphasis with gases was on the measurement of time-dependent processes. Following the early work of Slobodskaya in Russia and Stephens and Delaney in London, it was groups interested in the theoretical details of chemical kinetics (Cottrell, Bauer, Decius, etc) who attempted[1] to get meaningful analysis of the acoustic signals. These early measurements[1], up to c. 1970, were not particularly successful. The basis, of measuring the acoustic amplitude or its phase relative to the incident intensity modulations, was as for more recent measurements but suffered two main difficulties. The actual signals were not determined with the advantages of modern phase-sensitive equipment and were therefore more limited, and insufficient attention was paid to the proper calibration of the experimental system, i.e. the establishment of the phase characteristics of the system when no time delays were present due to gas relaxation.

The second difficulty was more surprising. Almost all the groups insisted on treating the relaxing gas as a simple two-state system, i.e. the excited state and the ground state. For example,[1] in methane in the infrared there are four fundamental bands; the one of highest energy, ν_3, was excited and instead of treating the system as a possible 'cascade' with the other fundamentals, at lower energies, involved, the tendency was to treat the data as if all the ν_3 energy would go directly to translational energy. It was the move to more realistic kinetics schemes, with the concomitant development in amplitude and phase models, which led to the clear establishment of the spectrophone as a technique in relaxation measurements.

Examining briefly a 3-state model,



following excitation to level 2, the phase lag ϕ measured in the spectrophone, relative to that of the modulated incident radiation, depends not only on the lifetimes of levels 1 and 2, τ_1 and τ_2 respectively, but also on the relative extent of routes a and b.

Manipulation of suitable level populations leads[2] to the expression

$$\tan\phi = [H \sin\theta_2 + L \cos\theta_1 \sin(\theta_2+\theta_1)]/[H \cos\theta_2 + L \cos\theta_1 \cos(\theta_2+\theta_1)]$$

where $\tan \theta_2 = \omega\tau_2$, $\tan \theta_1 = \omega\tau_1$ and H and L are parameters representing the heat yield pertinent to relaxation of states 2 and 1 respectively

$$[H = (k_b.\Delta E_{20} + k_a.\Delta E_{21}).\tau_2 \quad \text{and } L = k_a\, \tau_{21}.\Delta E_{10}].$$

It is commonly the case that $\tau_1 >> \tau_2$. This is true if the lowest excited state in an electronic manifold is a metastable triplet state, or, for vibrational states, if the lowest excited vibrational fundamental is the state coupled predominantly to translational movement. For this simplification the above expression for $\tan \phi$ reduces to

$$\tan \phi = \omega\tau_1/[1 + \frac{H}{L} + \frac{H}{L}\omega^2\tau_1{}^2]$$

from which it is straightforward to obtain the lifetime τ_1 and the best yield ratio H/L; this latter quantity turns out to be very important since very few techniques give information on the relative extents of different relaxation routes. The critical thing is that the spectrophone phase lag is dependent on parameters other than lifetimes.

This simple analysis of a 3-state problem can obviously be extended to a multi-state problem[3] with the only restriction, common to all such kinetic schemes, that with increasing complexity the number of unknown parameters goes up. This can be countered, to some extent, by using the many possible experimental variables, frequency of modulation, phase and amplitude information combined, gas pressure, additives, etc; we have, for example, treated a 6-state problem in vibrational relaxation and obtained most of the important decay parameters[4].

It is useful at this stage to mention some of the complications which arise in such measurements; the following topics will be discussed quantitatively in the lecture:- low frequency thermal diffusion to the walls, higher order acoustic modes, heat capacity effects, and particle density changes.

Experimental Systems (restricted to our own systems and results)

For accurate amplitude and phase measurements in the zeroth order acoustic mode we normally use a metal cell, roughly 1" in diameter and 1½" in length. The inlet gas valve is so arranged that, when closed, it completes a fully smooth cylinder; any hint of resonance always gives problems in obtaining accurate calibrations. The microphone normally used is a 1" B & K although other small microphones (some electret) have been used for particular measurements. Modulation of source intensity is by direct oscillator-amplifier control on lamp sources, or mechanical chopping, or by crystal Pockels cell. In addition to lamp sources, lasers have proved useful; a He-Ne laser at 3.39 µ for studying vibrational relaxation; He-Cd laser giving lines at 325 and 441 nm; Argon ion laser (20 watts cw) giving lines from c. 450 to 514 nm (plus some uv lines), dye laser for visible region tuning.

With narrow laser beams in an extracavity arrangement, either in a single- or multi-pass configuration, accurate phase calibration has proved possible but difficult. This is particularly so if, for chemical reasons, one requires an open cell (e.g. flowing gas) when Helmholtz resonances of even very low amplitude make reproducibility over a period of time difficult. Slight detuning of the lasers, especially the dye laser, leads to phase alterations presumably due to the varying number of passes in the laser cavity. No such problems are found, of course, in recording spectra. For very weak spectra an intracavity cell in the dye laser is used; using R6G Rhodamine dye (570-630 nm), for example, the power circulating in the dye laser cavity can be as high as 50 watts. For gases at > 100 Torr in the Brewster-windowed cell, transitions can be recorded with f-numbers in the range 10^{-12} to 10^{-13}, e.g. absorption bands in the visible spectrum of O_2 have been observed and common experience tells us how weak these must be.

Weak Transitions

There are obvious spectroscopic interests in being able to measure the characteristics of essentially forbidden transitions or in examining spectra of samples with very low vapour pressure and the optoacoustic technique has been used in this way. As a group, however, we are more interested in dynamic aspects of quantum states and in the theoretical basis of chemical kinetics. Chemical reactions, especially unimolecular processes, normally involve the activation of highly excited vibrational states. The examination of vibrational overtone and possible combination transitions in the visible region would give a better idea of the nature of these highly anharmonic states and from their widths give guidelines to the problem of vibrational energy randomisation in the absence of external perturbations such as collisions. From this type of work and the results of others in the liquid phase (Henry, Albrecht, etc) some conclusions can be reached.

(i) The spectra are dominated by a simple overtone pattern of the highest energy fundamental e.g. in benzene by overtones of the C-H stretch. This has led to the development of local mode theory.

(ii) In the gas phase rotational sub-structure is observed for molecules like C_2H_2 and CH_4 in the high overtones of the C-H stretch (0-6 transition comes at around 600 nm) and no fast coupling of the prepared state with the high density of other vibrational states is observed.

(iii) For larger molecules, and also some substituted methanes, no rotational structure is observed and, from widths of c. 100 cm^{-1}, it can be deduced that the lifetime of the prepared state is c. 0.1 to 1 ps. In these cases non-collisional energy redistribution is obviously exceedingly fast and theories based on fast randomisation of energy, and thus statistical assumptions, are given some backing.

(iv) When molecules are studied, e.g. 1,3 pentadiene, which have an activation energy for reaction below the excitation energy (at $\sim$ 600 nm) the width for the C-H overtone is of the same order as in benzene, i.e. the rate-determining process is vibrational energy redistribution and not immediate chemical bond rupture.

(v) The possibility has been suggested of developing a 'vibrational photochemistry' with excitation, say, in a complex molecule to different CH (or OH) overtones leading to different energy pathways and thus to different products. If the fast energy redistribution in fact infers a fast randomisation, such selective photochemistry would appear to be ruled out.

Examples of Relaxation Problems Studied in the Spectrophone

An indication of the problems and the results is given here with optoacoustic details left for the lecture.

(A) Considerable interest has been shown in the possibility of an I atom laser using the $I(^2P_{3/2}) \longleftarrow I(^2P_{1/2})$ transition. If a molecule XI is dissociated with the resulting populations $I(^2P_{1/2}) > I(^2P_{3/2})$ then the chances are good for an efficient lasing system. We have examined a number of alkyl iodides, CH_3I, C_2H_5I, C_3H_7I, CD_3I, CH_2I_2, measuring the branching ratio $[^2P_{1/2}/^2P_{3/2}]$ as a function of excitation wavelength[9], thus establishing in which excitation energy regions one can expect lasing action. The extent of production of these atomic states also allows one to determine the presence of separate electronic states within the wide, uninformative shape of the normal absorption spectrum. Although the lifetimes of excited atomic states are measured the above more interesting results come from the heat yield ratio H/L.

(B) At fairly low total energy, transfer of vibrational energy between the vibrational quantum states does not take place intramolecularly but involves collisions. Very little is known about the lifetime of such quantum states, other than the lowest excited vibrational fundamental, and even less is known about the routes followed in such relaxations. For example, if one excites the ν_3 level of CH_4 (3020 cm^{-1}) what role do the other available vibrational levels play in the deactivation which eventually leads to translational energy? [ν_1 2917 cm^{-1}, ν_2 1533 cm^{-1}, ν_4 1306 cm^{-1}, $2\nu_2$ 3072 cm^{-1}, $\nu_2 + \nu_4$ 2823 cm^{-1}, $2\nu_4$ 2600 cm^{-1}]. The results of our examination using a He-Ne laser (in conjunction with infrared emission measurements) are as follows; (i) the ν_3 and ν_1 levels couple extremely quickly (close to collisional) and act as one level, (ii) (ν_3, ν_1) decays quantitatively to $2\nu_4$ (why are the levels $2\nu_2$ and $\nu_2 + \nu_4$, which are energetically available, missed out? some collisional symmetry selection rule?), (iii) $2\nu_4$ decays through collision to two molecules each in ν_4, (iv) ν_4 and ν_2 reach a fast equilibrium, and (v) the final step to translational energy is $(\nu_4, \nu_2) \longrightarrow$ ground state. Rate constants have been measured for all these steps. By carrying out extensive measurements on CH_4 with a large variety of additive collisional partners, some idea of the most likely routes in vibrational-vibrational processes starts to emerge. Such information is, of course, necessary for a full theoretical treatment of reaction kinetics.

(C) The study of electronic states in aromatic molecules and the associated radiationless processes has been well documented, but, perhaps surprisingly, the lowest energy electronic state, a triplet, has not been well characterised with respect to its dynamic properties in the vapour. The first direct determination[10] of benzene triplet lifetimes in the vapour were spectrophone results. Two interesting points emerge from further optoacoustic work on these systems.
(a) The triplet lifetime is quite short (10^{-3} s or less) partly because in some cases (benzene but not many substituted benzenes) there is a strong collisional interaction between the triplet and ground states. In most cases the vapour phase lifetime is shorter than that measured in solid solution at the same temperature. In terms of perturbation theory this is intriguing.
(b) The higher the vibrational content in the triplet state the faster it decays to the ground state; this means that when the triplet state is formed by intersystem crossing from a higher singlet state, it is possible that the vibrationally relaxed triplet state is never formed. In looking for long-lived triplet states (relative to the much shorter-lived excited singlet states) it is possible, then, that non-observance is not due to the lack of formation of triplet states but is due to the very rapid coupling (on the same time-scale as the decay of the excited singlet states) of the vibrationally excited triplet state with the ground state.

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