PHYSICS

Calculations of the Einstein A Coefficient for the 18 cm Transition of OH

LIDE[1] has pointed out that my calculation[2] of the Einstein A coefficient for the 18 cm transition of OH is twice the correct value. This calculation referred to a representation in which hyperfine splitting is not included. I agree with Lide, who notes that the dipole factor $|\mu_A|^2$ was correctly calculated in ref. 2, but that the statistical weight was too small by a factor of two.

Lide also suggested some numerical inconsistencies existed in an otherwise correct calculation by Turner for the Einstein A coefficients of the individual hyperfine transitions in the ground state. Lide did not account, however, for differences in the frequencies of the four hyperfine transitions, and when these are included, the results of Turner follow. This means that $(A_{1667}/\nu_{1667}^3) + (A_{1720}/\nu_{1720}^3) \approx (A_{1665}/\nu_{1665}^3) + (A_{1612}/\nu_{1612}^3)$ is a considerably better approximation than $A_{1667} + A_{1720} \approx A_{1665} + A_{1612}$. Actually, as Lide has privately remarked, the former of these relations is itself limited in accuracy by the first order approximation made in the hyperfine calculation, that the nuclear spin perturbation is much smaller than the spacing between unperturbed levels in the Λ doublet. A higher order matrix element calculation would, however, affect the matrix elements by only about 0·1 per cent, which is much smaller than the inaccuracies introduced by taking the four hyperfine transition frequencies to be the same. I think therefore that the results given in ref. 2 are correct to well within present needs, namely:

$$A_{1667} = 7 \cdot 712 \times 10^{-11}$$
$$A_{1665} = 7 \cdot 116 \times 10^{-11}$$
$$A_{1612} = 1 \cdot 291 \times 10^{-11}$$
$$A_{1720} = 0 \cdot 942 \times 10^{-11}$$

Conversely, it is especially the relative inaccuracies among the four hyperfine A coefficients as given by Lide that may be large enough eventually to affect theoretical attempts to interpret anomalous OH emission and absorption in the interstellar medium.

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[2] Turner, B., Nature, 212, 184 (1966).

Nucleation of Freezing by Cavitation in Supercooled Liquids

I HAVE proposed[1] that the nucleation of freezing by cavitation is caused, in all supercooled liquids, by the high compressions generated near the surfaces of collapsing cavitation bubbles. I have assumed[1] that the compression is isentropic. Recently, Hunt and Jackson suggested that this assumption is erroneous and that the Rankine–Hugoniot relations across a shock wave front are a more realistic representation of the thermodynamic behaviour of the liquid during cavity collapse[2]. Because the theory of nucleation that I propose is apparently[2] dependent on the validity of the isentropic assumption it is necessary to decide which of the two thermodynamic states is more appropriate.

Hunt and Jackson support the Rankine–Hugoniot relations, and therefore their point of view is clearly based on the belief that shock waves occur during the collapse of cavitation bubbles. Shock waves, however, cannot occur at this stage of the bubble wall motion, because the conditions for generating shock waves do not arise[3]. Only a simple compression occurs at this time. A shock wave emanating from the collapse centre of the bubble does indeed form[3], but only at a later stage after the collapse and its associated process of compression have been completed. This process of compression can deviate from the isentropic condition through viscosity and heat conduction. The viscous effects are usually acknowledged, however, to be negligible and I have shown[1] that there is not much time for heat conduction. If heat conduction does occur then the conditions for creating nuclei under high pressure would only be further improved. There therefore seems to be no reason to believe that the isentropic condition is not a suitable assumption.

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[1] Hickling, R., Nature, 206, 4987 (1965).
[2] Hunt, J. D., and Jackson, K. A., Nature, 211, 5053 (1966).
[3] Hickling, R., and Plesset, M. S., Phys. Fluids, 7, 1, 7 (1964).

CHEMISTRY

Identity of the C₅₀-Carotenoid Dehydrogenans-P439 and Sarcinaxanthin

A UNIQUE C_{50}-carotenoid has been isolated from the Gram-positive bacterium, Flavobacterium dehydrogenans Arnaudi[1], and the compound partially characterized[2,3]. Subsequent investigations have revealed that the carotenoid, designated dehydrogenans-P439, commonly occurs in pigmented Gram-positive bacteria[4]. The carotenoid sarcinaxanthin, originally obtained from the bacterium Sarcina lutea, has previously been characterized only from its melting point, electronic spectra in various solvents, partition behaviour and adsorptive property[5]. These and subsequent data[5,6] showed a neurosporene-like absorption spectrum but a more polar behaviour than neurosporene, and a number of investigators have used these very general properties to claim the presence of sarcinaxanthin in algae[7] and bacteria other than Sarcina[8,9]. Dehydrogenans-P439 has the general characteristics of sarcinaxanthin[10] and the comparative investigation reported here has shown the two carotenoids are identical.

In order to determine the chemical nature of dehydrogenans-P439 we used the carotenoid isolated from F. dehydrogenans (the procedures have been described elsewhere[3]). Dehydrogenans-P439 crystallized from acetone–petroleum ether as red needles, with a melting point of 154°–155° C (uncorrected; evacuated capillary tube) which is in satisfactory agreement with the melting point previously reported for sarcinaxanthin[5]. Dehydrogenans-P439 was further characterized from stereomutation investigations (Table 1), the preparation of a monoacetate and diacetate by acetylation with acetic anhydride

Table 1. ABSORPTION MAXIMA IN VISIBLE LIGHT OF DEHYDROGENANS-P439 AND SARCINAXANTHIN

Carotenoid	Stereoisomer		Hexane			Absorption maxima (mμ) in Methanol			Carbon disulphide		
Dehydrogenans-P439	Trans	(304)	416	439·5	470	416	439	469	440	469	499
	Neo U		415	436	465	414	436	465			
	Iodine catalysed equilibrium mixture	(394)	416	438	468	415	437	467			
Sarcinaxanthin*		(415)	440	469					436	466·5	499
Sarcinaxanthin	Trans					415	439	469			
	Neo U					412	436	466			
	Iodine catalysed equilibrium mixture					414	437	468			

* Takeda and Ohta[5].