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THE CARBONATE, $Co_3^{-\bullet}$, IN SOLUTION STUDIED BY RESONANCE RAMAN SPECTROSCOPY

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The carbonate radical ($CO_3^{-\bullet}$) is of biological significance acting as an intermediate in free radical-mediated damage and is capable of oxidising amino acids and proteins. In order to distinguish between the four possible structures of $CO_3^{-\bullet}$, nanosecond time-resolved resonance Raman (TR^3) experiments were undertaken. Photolysis of persulphate at 250 nm generated the $SO_4^{-\bullet}$ radical which then oxidised sodium carbonate. Resonance Raman spectra of the resulting $CO_3^{-\bullet}$ radical were obtained using a probe wavelength of 620 nm. Point group theory calculations and interpretation of the TR^3 spectra suggest that the radical has C_{2v} molecular symmetry.

Keywords: Carbonate; radical; Raman

INTRODUCTION

It has recently been proposed that carbonate radicals may be intermediates in free radical-mediated damage in biological systems. The carbonate radical is a powerful oxidant with a one electron reduction potential of 1.59 V at pH 12, and is capable of the one-electron oxidation of several amino acids and proteins [1, 2].

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Peroxynitrite, an important contributor to oxidative stress, reacts with carbon dioxide and the carbonate radical is a possible product of this interaction [3]. In phagosomes which contain high levels of bicarbonate, the carbonate radical formed from scavenging of hydrogen peroxide derived $^{\bullet}OH$ may be a significant contributor to radical mediated damage [4]. The carbonate radical has been produced and identified by laser flash photolysis [5] which shows it to have a broad featureless absorption spectrum with λ_{max} 600 nm and $\varepsilon_{600\,nm} = 200\,dm^2\,mol^{-1}$.

EXPERIMENTAL

Solutions of sodium persulphate (0.5 M) and sodium carbonate(0.1 M) in water at pH 12.2 were photolysed at 250 nm with the output of a frequency-doubled dye laser (Lambda-Physik FL3002) (ca. 2 mJ, 10 ns pulse length) pumped by a Lumonics XeCl excimer laser. A Continuum Sunlite OPO was used as the probe laser pulse (620 nm, ca. 1.5 mJ, 5 ns pulse length). The sample was recirculated through a quartz sample tube (2 mm i.d.) and Raman scatter collected at 90° and focused onto the entrance slit of a Spex Triplemate 1877 spectrometer. The spectra were recorded on a back-illuminated liquid nitrogen cooled CCD camera (Princeton Instruments) and were typically accumulated over 20,000 laser pulses at 10 Hz repetition rate. Spectral subtractions and other manipulations were performed using the Princeton CSMA software. Apparatus and chemicals were either AnalaR grade or similar and water was obtained from a Millipore Milli Q.

RESULTS AND DISCUSSION

Possible structures of the carbonate radical are shown in Figure 1. The correlation table (Tab. I) shows the symmetry of the vibrations for each of these structures. The observed TR[3] spectra of $CO_3^{-\bullet}$ (Fig. 2) contains five principal bands indicating at least five separate vibrational modes for $CO_3^{-\bullet}$. The frequencies of these bands are given in Table II together with depolarisation ratios showing the spectrum

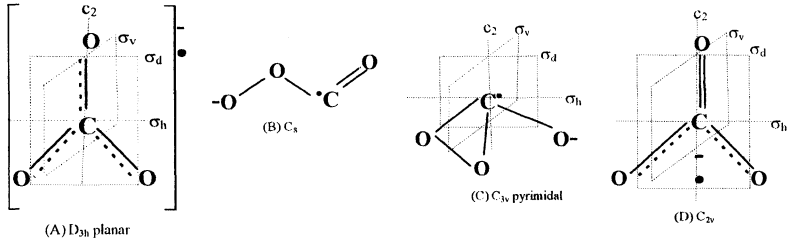

FIGURE 1 Possible structures of the carbonate radical.

TABLE I Correlation table of possible point groups for the carbonate radical [6]

		Vibration			
Structure	*Point Group*	υ_1	υ_2	υ_3	υ_4
A	D_{3h}	$A_1'(R)$	$A_2''(IR)$	$E'(R, IR)$	$E'(R, IR)$
B	C_s	A_1 (R, IR)	A'' (R, IR)	$A'(R, IR)$, $A'(R, IR)$	$A'(R, IR)$, $A'(R, IR)$
C	C_{3v}	A_1 (R, IR), A_1 (R, IR)	A_1 (R, IR), A_1 (R, IR)	$E'(R, IR)$	$E'(R, IR)$
D	C_{2v}	A_1 (R, IR)	B_1 (R, IR)	A_1 (R, IR), B_2 (R, IR)	A_1 (R, IR), B_2 (R, IR)

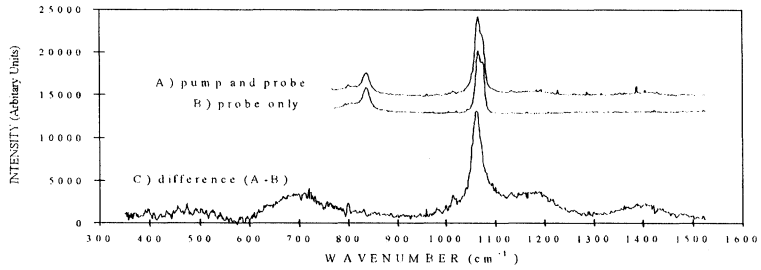

FIGURE 2 Time-resolved resonance Raman spectrum from laser photolysis of solutions of sodium persulphate and sodium carbonate at pH 12.3. (A) pump/probe (250/620 nm) with time delay of 1 μs, (B) probe laser (620 nm) only, (C) difference spectrum (A − B).

TABLE II Frequency shifts (relative wavenumber) of carbonate radical in water. Figures in brackets denote depolarisation ratios

Carbonate radical in H_2O	*Assignment*
463 (−)	($\upsilon_2(B_1)$) C—O out-of-plane bend
703 (0.10)	($\upsilon_4(A_1)$) C—O symmetric in-plane bend
1063 (0.28)	($\upsilon_1(A_1)$) C—O symmetric stretch
1159 (0.49)	($\upsilon_3(A_1)$) C—O symmetric stretch
1365 (0.65)	($\upsilon_4(B_2)$) C—O anti-symmetric stretch
1410 (0.65)	($\upsilon_4(B_2)$) C—O anti-symmetric stretch

to include two symmetric and two anti-symmetric vibrations. From these results, the structure belonging to the C_s point group may be eliminated since it predicts only symmetric vibrations. The structure with D_{3h} symmetry may also be rejected because it has only three Raman active vibrations compared with the five observed bands. Similarly the structure with C_{3v} symmetry should have only four Raman active vibrations and may also be eliminated. ESR spectra also do not support the C_{3v} structure since they reveal low un-paired electron density of the central carbon atom [7]. This leaves the structure with C_{2v} symmetry. This assignment indicates six Raman active modes of which we observe five. It is expected that the two out of plane C—O bending modes would be weak if the molecule has a planar structure dependant on sp^2 hybridisation of the carbon atom as favoured by both theory [8] and ESR spectroscopy.

Calculations performed at the UMP2 level using the basis set aug-cc-pVTZ (G Scholes, private communication) also predict a planar C_{2v} structure for a gas phase molecule. However, the calculated frequencies were not in agreement with experimental data reported here, and it is possible that solvent perturbation may account for some of the discrepancy. A bridged structure involving an O—O bond has been proposed for the neutral CO_3 species, but in $CO_3^{-\bullet}$ such a structure would require significant unpaired spin at the carbon atom , which is not the case as discussed above.

The transient resonant Raman spectrum of the carbonate radical is shown in Figure 2 with the band positions, depolarisation ratios and assignments given in Table II. Separate experiments assigned the bands at 835 and 1074 cm^{-1} as the non-resonant Raman bands of the persulphate ion and the 1065 cm^{-1} band as the carbonate (CO_3^{2-}) ion. Spectra were collected over the higher (1500 – 2200 cm^{-1}) wavenumber range but no other bands were observed in this region. The assignments in Table II are based upon vibrational analysis of the spectrum of HCO_3^- and CO_3^{2-} [8]. The spectrum has one strong band at 1063 cm^{-1} which is assigned as the symmetric C—O stretch. Weaker and broader bands are observed at 463 cm^{-1} (assigned as the C—O out-of-plane bend), at 703 cm^{-1} (the symmetric C—O in-plane bend), and at 1159 cm^{-1} (symmetric C—O stretch). The vibration at 1159 cm^{-1} results form the symmetric vibration involving the stretching of the C=O bond and shortening of the C—O bonds.

Since relatively strong but perhaps unequal solvent interactions may be expected with the electronegative oxygen atoms of the C—O bonds, the symmetry of this vibration may be reduced, accounting for the depolarisation ratio of 0.49 which approaches the value expected for an anti-symmetric vibration. The band at 1400 cm^{-1} assigned to an anti-symmetric C—O stretch is very broad and using a spectral fitting programme may be resolved into the two bands at 1365 and 1410 cm^{-1} shown in Table II. The splitting of this band into a doublet is attributed to the interaction of the carbonate radical with the surrounding solvent and is also observed in the carbonate ion (CO_3^{2-}) [8] and alkali metal nitrates [9].

CONCLUSIONS

The data indicates that the Raman spectrum of the carbonate radical ($CO_3^{-\bullet}$) formed by one-electron oxidation of carbonate contains five Raman active vibrations and strongly suggest the radical has planar C_{2v} molecular symmetry.

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