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Self broadening of OCS rotational lines in the microwave region

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Self broadened widths of rotational lines in the microwave region of OCS have been re-studied using the new interruption function under the Anderson's theory which somewhat resolves the discrepancies in theoretical and experimental values. The quadrupole moment of OCS has thus been re-evaluated to be 4.25 ± 0.19 DA. The Rabitz effective potential used in Murphy Boggs theory gives too low values of line width parameters.

The collision broadening of OCS has been extensively studied experimentally as well as theoretically. The measured and calculated values of the line width parameters have been compiled in a review by KRISHNAJI[1]. Rabitz[2] has lso reviewed different theoretical approaches and experimental techniques. There are discrepancies in the measurement of line-width parameters of OCS and thereby in the evaluation of its molecular quadrupole moment. The results are different even with the same technique using different samples of OCS for J_{1-2} line (see Table 1).

Anderson's perturbation theory[3] as developed by Tsao and Curnutte[4] and Krishnaji and Srivastava[5], and Murphy-Boggs theory[6] have been used to explain the line width data. Most recently JOHRI and SRIVASTAVA[7] have proposed a new interruption function in perturbation theory in molecular collisions. This function resolves some of the theoretical and experimental discrepancies and takes into account both the elastic and inelastic collisions unlike MB theory where phase shift has been ignored.

Self broadened width of OCS J_{1-2} line at 24325.9 MHz has been remeasured on a double modulation microwave spectrometer using the techniques of first derivative and second derivatives after distilling the sample of OCS twice under vacuum. The experimental details are the same as described earlier[8]. The values thus obtained are given in table 1.

Table 1. Linewidth parameter for $J_{1\text{-}2}$ line of OCS as measured by different workers

Workers		Linewidth parameter (MHz/Torr)	Ref.
Johnson and Slager	(1952)	6.10 ± 0.35	(14)
Feeny et al	(1954)	6.44 ± 0.18	(15)
Dymanus et al	(1960)	6.45 ± 0.15	(16)
Britt and Boggs	(1966)	6.25 ± 0.18	(17)
Krishnaji and Srivastava	(1967)	6.22 ± 0.20	(8)
Berendts and Dymanus	(1968)	6.28 ± 0.03	(18)
Battaglia et al	(1969)	6.15 ± 0.20	(19)
Olson et al	(1973)	6.07 ± 0.14	(20)
Wang et al	(1973)	5.25 ± 0.50	(21)
Mehrotra	(1975)	5.27 ± 0.16	(22)
This work	(1976)		
	First derivative	6.06 ± 0.21	
	Second ,,	6.35 ± 0.25	

The calculations using new interruption function in the formal theory due to Anderson have been done for OCS for different transitions considering dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, quadrupole-dipole and dispersion interactions. Method of calculations is the same as given in earlier papers of the author[6]. The use of this function gives values of line width parameters lower than those obtained from Anderson's approximation no. 2 and are comparable with MB theory (see table 2). The new interruption

Table 2. Measured and calculated widths for different transitions of OCS and its molecular quadrupole moment from MB theory and from present interruption function

Transition	Measured widths[20] (MHz/Torr)	Calculated width (MHz/Torr)				θ (DÅ)	
		ATC ($\theta^2=0$)	MB ($\theta=1.57$ DÅ)	Rabitz	Present Function	MB	Present Function
1–2	6.15	6.20	5.73	4.21	5.81	4.55	3.85
2–3	6.25	6.24	5.80	4.26	5.87	4.90	4.10
3–4	6.37	6.34	5.88	4.36	5.98	5.25	4.50
4–5	6.43	6.39	5.97	4.49	6.08	5.10	4.25
5–6	6.52	6.48	6.02	4.56	6.14	5.15	4.40
				Average θ_{OCS}		4.99±0.21	4.25±0.19

function gives nearly 15% lower values of quadrupole moment than MB theory. The mean value of $\theta_{ocs} = 4.25 \pm 0.19$ DÅ obtained by new interruption function agrees with that obtained by Taft and Dailey[9] ($\theta_{ocs} = 4.2$ DÅ) but higher than that obtained by Flygare[10] ($\theta_{cs} = 1.76$ DÅ). Recently Rothenberg and Schaefer[11] have pointed out that quadrupole moment of O_3 determined by Flygare et al may not be reliable. This has created doubt on such a low value of quadrupole moment of OCS reported by Flygare[10]. The use of Rabitz effective potential[12] in MB theory gives too low values of the line width parameters, but in behaviour is qualitatively similar to MB theory as has also been shown by Mehrotra and Boggs[13].

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