Pressure broadened calculations of the OCS $J = 1 \to 2$ line by non-polar perturbers

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Abstract. Microwave spectral line widths of the transition $J = 1 \to 2$ of OCS perturbed by non-polar perturbers, n-hexane, cyclohexane, n-heptane, carbon disulphide, carbon tetrachloride and benzene have been calculated using a recent theory of Mehrotra and Boggs.

1. Introduction

Recently Mehrotra and Boggs (1977) formulated a more general theory of the width and shift of microwave absorption lines under impact approximation with elastic as well as inelastic collisions being considered more rigorously. This theory which is an improvement over those formulated earlier (Anderson 1949; Murphy and Boggs 1967; Gordon 1966) has been successfully applied to pure rotational transitions of the OCS–OCS, OCS–He and OCS–Ar systems. In this paper we have applied the theory to explain the line width of the $1 \to 2$ transition of OCS perturbed by non-polar gases, viz n–hexane (C_6H_{14}), cyclohexane (C_6H_{12}), n–heptane (C_7H_{16}), carbon disulphide (CS_2), carbon tetrachloride (CCl_4) and benzene (C_6H_6).

2. Theory

The line width parameter is given by

$$\triangle \nu = N \sum_{J_2} \rho_{J_2} \int_0^\infty db\, b \int_0^\infty d\nu\, \nu f(\nu)\, [1 - \exp\left(-\tfrac{1}{2}\Gamma_{J_iJ_2} - \tfrac{1}{2}\Gamma_{J_fJ_2}\right) \times$$

$$\cos(\phi_{J_iJ_2} - \phi_{J_fJ_2})], \tag{1}$$

where i and f are the initial and final states of the absorbing molecule, 2 denotes the state of perturbing molecules and N is the number density of the perturbing molecules. $f(\nu)$ is the Maxwellian probability distribution for a relative speed between absorbing

and perturbing molecules. ρ_{J_2} is the Boltzman distribution of the perturbing molecules, b is the impact parameter, Γ and ϕ are collision weightage functions which are dynamically related to the interaction between two molecules. The method of calculation of these functions are given by Mehrotra and Boggs (1977).

3. Results and discussion

All computations were carried out on a CDC 3600 computer. The calculated values together with the experimental values (Pandey *et al* 1971) are given in table 1. The interaction considered in the calculations is of dispersion type. Table 1 shows that the calculated values of the line widths of the OCS—C_6H_{14}, OCS—C_6H_{12}, OCS—C_7H_{16} and OCS—C_6H_6 are lower than the experimental value, to an extent of 12·5%, 7·1%, 14·1% and 26·6% respectively. However, in the OCS—CS_2 system, the calculated and experimental values show good agreement. The contributions due to the quadrupole moment of the perturber which are not expected to be significant, have not been included in our calculations. Carbon tetrachloride is a spherical top molecule and belongs to T_d point group. The calculated value of line width in OCS—CCl_4 collision is about 20·6% more than the experimental linewidth. This discrepancy may be due to the non-vanishing dipole moment of CCl_4 in the excited vibrational states as shown by Mizushima and Venkateswarlu (1953). Ozier (1971) and Ozier *et al* (1970) determined dipole moment of methane from stark effects of molecular beam resonance in the ground vibrational state and obtained a value $|\mu| = (5\cdot38 \pm 0\cdot10) \times 10^{-6}$ Debye. This shows that the magnitude of the rotation-induced dipole moment in the tetrahedral molecule is smaller in the ground vibrational state ($\sim 10^{-5}$ Debye) than in the excited state ($\sim 10^{-2}$ Debye). Part of the discrepancy between the calculated and the experimental line width parameter can be explained by the non-vanishing dipole moment of CCl_4 in the ground vibrational state. However, the effect of the rotation-induced dipole moment in CCl_4 in its ground state has not been included in the present calculations.

Table 1. Calculated values of line widths for OCS J=1 → 2 line considering dispersion 1 and dispersion 2 forces

Absorber-perturber	Measured[a] ($\triangle v/p$) MHz torr^{-1}	Calculated ($\triangle v/p$) MHz torr^{-1}	
		MEB[b]	ATC # 2[c]
OCS − C_6H_{14}	4·17 ± 0·30	3·65 (12·5)	4·14 (0·7)
OCS − C_6H_{12}	4·10 ± 0·36	3·81 (7·1)	4·27 (−4·1)
OCS − C_7H_{16}	4·83 ± 0·32	4·15 (14·1)	4·66 (3·5)
OCS − CS_2	3·37 ± 0.28	3·30 (2·1)	3·95 (−17·5)
OCS − CCl_4	3·00 ± 0·13	3·62 (−20·6)	4·10 (−37·0)
OCS − C_6H_8	5·14 ± 0·34	3·77 (26·6)	4·22 (17·9)

[a]Pandey *et al* (1971); [b]MEB Mehrotra and Boggs theory; [c]Tsao and Curnutte (1962); Paranthesis values indicate percentage deviation from the measured values.

It is thus concluded taking into account the elastic and inelastic collisions that the Mehrotra and Boggs theory is reasonably good to interpret the pressure broadening data and that the collision interruption function is somewhat complex. This theory gives smaller widths than the Anderson-Tsao-Curnette theory which also takes into account the effect of elastic and inelastic collisions.

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