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Microwave spectroscopy of free OH radicals in the 37 GHz range = determination of mean collision cross-sections with various gases

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Résumé. — Nous avons poursuivi l'étude expérimentale des collisions de OH avec quelques gaz : H_2O , NO_2 , CH_3Cl , N_2 , H_2 , He et obtenu des sections efficaces moyennes de collision. L'accord avec les valeurs théoriques est en général assez satisfaisant. On a calculé une nouvelle valeur du moment quadrupolaire de N_2 .

Abstract. — The experimental study of OH collisions with various gases (H_2O , NO_2 , CH_3Cl , N_2 , H_2 , He) was continued and mean collisions cross-sections were obtained. In general, the agreement with theoretical values is satisfactory. A new value for the quadrupole moment of N_2 is calculated.

Values for mean collision cross-sections of OH with various gases are given in previous papers [1], [2]. They were experimentally determined from measurements of line-width or from studies of the saturation of hyperfine transitions in the A doubling of the $2\pi_{3/2}$, $J = 7/2$ state. These studies were performed in the $2\pi_{3/2}$, $J = 11/2$ state using a spectrometer in the 37 GHz range ($F = 6 \rightarrow 6$ transition). When a foreign gas is added at various partial pressures, it is possible to study the collision of OH with this gas. The broadening parameter, designated a , is the ratio of the increase $\Delta\nu$ in the signal half width ν at half intensity over the variation Δp in partial pressure. OH production is obtained either by cracking H_2O or from the $\text{NO}_2 + \text{H}$ reaction; an accurate analysis of the results has shown that some gases appreciably modify OH production conditions and this could explain the dispersion of values obtained under different production conditions [3]. So such measurements are not taken into consideration. Production by cracking H_2O is generally better because there are not so many recombination products.

Experimental results (Table I, columns 1 and 2) were inferred from a linear least-squares fit of a large number of measurements. Errors are typically about 7 %. Because of the dimensions of the measurement cavity, the contribution of collisions on the wall to signal broadening is negligible.

Theoretical values for the mean collision cross-section σ_{th} were obtained from the Anderson and Tsao-Curnutte theory [4, 5]. Interactions proceed

Table I. — *Experimental and theoretical values of the broadening parameter $\Delta\nu/p$, and collision cross-section for OH with foreign gases.*

	$\left(\frac{\Delta\nu}{p}\right)_{\text{exp}}$ MHz/torr	σ_{exp} 10^{15} cm^2	$\left(\frac{\Delta\nu}{p}\right)_{\text{th}}$ MHz/torr	σ_{th} 10^{15} cm^2
CH_3Cl	4.6	12	4.75	12.2
H_2O	6.6	14	7.31	15.5
NO_2	4.5	11	1.14	2.88
N_2	3.4	7.9	—	—
H_2	2.3	2.2	2.04	1.96
He	1.4	1.8	0.88	1.13

from dipole and quadrupole moments and also induced moments. For a given type of interaction, the probability $S(b, J_2)$ for a complete interruption of the absorbing molecule radiation with the disturbing molecule in the J_2 state (b is the impact parameter) allows σ to be calculated. When several types of interaction coexist, these probabilities are added; as a general rule, long distance interactions are more important than short ones, which are consequently often negligible [4].

OH- CH_3Cl interaction is of the dipole-dipole type; there is a satisfactory agreement between calculated and measured values of σ .

To study OH- H_2O collisions, the OH radical was produced by cracking H_2O ; because of low efficiency

(about one per cent), the partial pressure of H_2O is nearly equal to the total pressure in the cavity. The value of σ_{th} corresponds to dipole-dipole interaction; the static dipole moment μ_s was taken as equal to 1.8×10^{-18} cgs, although, according to different authors, the given values differ by 10 %. We also calculated dipole-quadrupole interactions, and in agreement with other authors [7], found that its contribution can be neglected.

Studies of OH-NO_2 collisions were performed for $\text{NO}_2 + \text{H}$ production. The dipole moment of NO_2 is weak and its numerical value varies, according to several authors, between 0.3 and 0.59×10^{-18} cgs [8]. σ_{th} (Table I, column 3-4) is considerably smaller than σ_{exp} . However, dipole-dipole interaction was not taken into account, though dipole-induced dipole interaction also exists; because the polarisability of NO_2 in this frequency range is not known, we cannot calculate this interaction. Calculations using a typical value for this polarisability lead to a higher contribution for σ_{th} than with dipole-dipole interac-

tion, σ_{th} approaching more nearly the value deduced from experiment. In other respects, it should be observed that NO_2 is in chemical equilibrium with N_2O_4 : at a temperature of 20 °C, there is about 60 % N_2O_4 at air pressure but only 1 % at a pressure of 1 torr. Hence, it is convenient to measure the physical constants of NO_2 at low pressure.

OH-N_2 interaction is of dipole-quadrupole type. According to 14 authors, the numerical value of the quadrupole moment Q of N_2 varies between 1.5 and 6×10^{-26} cgs [9]. So it is preferable to deduce Q from σ_{exp} ; the value $Q = 3.3 \times 10^{-26}$ cgs was obtained.

OH-H_2 interaction is also of dipole-quadrupole type; OH-He interaction is of the dipole-induced dipole type. These interactions are at very short distance, particularly the latter, and experiments are less satisfactory, as Anderson has remarked [4].

At the same time we made a study of saturation in the cavity, which will allow double irradiation experiments to be performed.

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