Line Widths in the Pure Rotational Raman Spectra of Hydrogen and Deuterium Self-Broadened and Broadened by Foreign Gases

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The pressure-broadening coefficients for the self-broadened $S_0(0)$, $S_0(1)$ and $S_0(2)$ pure rotational Raman lines of hydrogen and the $S_0(0)$ to $S_0(4)$ lines of deuterium were determined experimentally over the pressure range 1–100 bar and the temperature range 90–375 K. Broadening coefficients were also determined for the same lines in hydrogen and deuterium perturbed by helium, argon, oxygen, nitrogen, carbon monoxide and hydrogen chloride over the pressure range 2–100 bar, with a partial pressure of the host gas of 1 bar and a temperature of 293 K. In addition, the $S_0(0)$ pure rotational line of deuterium broadened by carbon monoxide and nitrogen was studied over the same pressure range and a temperature range of 100–293 K. The results are discussed and compared with those of previous studies in the literature.

INTRODUCTION

Information on the line widths of rotational Raman lines and their variation with pressure and temperature is needed for the application of CARS to the determination of species concentration and temperatures in gases and flames. Previous results from this laboratory have been published for the self-broadening of five rotational lines of oxygen and nitrogen[1] and of carbon monoxide and hydrogen chloride[2] and some foreign gas broadening of oxygen, nitrogen and hydrogen.[3] In this paper we present results for the self-broadening of the pure rotational Raman lines of hydrogen and deuterium over the pressure range 1–100 bar and the temperature range 90–375 K and the foreign gas broadening of the same rotational lines by helium, argon, oxygen, nitrogen, carbon monoxide and hydrogen chloride over the pressure range 2–100 bar with partial pressure of the host gas of 1 bar at 293 K.

There have been several previous studies of the self-broadening of the pure rotational Raman lines of hydrogen and deuterium. May *et al.*[4] investigated the broadening of the $S_0(0)$ and $S_0(1)$ pure rotational Raman lines of $^1H_2$ over the pressure range 100–2000 bar at room temperature. Cooper *et al.*[5] studied the self-broadening of the $S_0(0)$ and $S_0(1)$ rotational Raman lines of $^1H_2$ over the range 1–100 amagat and observed a minimum line width due to Dicke narrowing at about 100 amagat. At greater densities a linear increase in line width with density was found. The broadening coefficients for the $S_0(0)$ and $S_0(1)$ lines were not in agreement with the earlier values of May *et al.*[4] and the theoretical studies of van Kranendonk.[6] However, in a redetermination of the self-broadening coefficients for these rotational lines, Cooper *et al.*[7] obtained values which were an order of magnitude larger than the previous results.[5] There was now good agreement for the $S_0(0)$ rotational line, but the self-broadening coefficient for the $S_0(1)$ line was still lower than in the earlier determination.[4] Later, Gupta *et al.*[8] measured the self-broadening coefficient of the $S_0(1)$ Raman line of $^1H_2$ and concluded that the broadening coefficient was independent of polarization orientation.

The importance of resonance collisions in rotational energy transfer has been investigated by Keijser *et al.*,[9] who studied the self-broadening of the $S_0(0)$–$S_0(4)$ rotational Raman lines of $^1H_2$, $^1H^2H$ and $^2H_2$. Using different concentrations of *ortho*-$^1H_2$ and *para*-$^1H_2$, it was found that the line widths of the $S_0(1)$ and $S_0(3)$ lines decreased initially with increase in concentration of *para*-$^1H_2$. However, at high *para*-$^1H_2$ concentrations, the $S_0(0)$ and $S_0(2)$ line widths were resonantly enhanced. It was estimated that resonance enhancement contributed about 40% to the line width in $^1H_2$. The results for $^2H_2$ were similar to those for $^1H_2$, but the $^1H^2H$ line widths showed a classical J dependence.

Further studies of the rotational line self-broadening of $^1H_2$, $^1H^2H$ and $^2H_2$ were carried out over the temperature range 25–300 K by Knaap *et al.*[10] The room temperature results were in good agreement with those of Keijser *et al.*[9]

Dayan and Viennot[11] measured the line widths of the $S_0(1)$ rotational line of $^1H_2$ perturbed by nitrogen, ethene and carbon dioxide at room temperature. The line broadening was found to increase in the order $N_2 < C_2H_4 < CO_2$ and could be explained in terms of dominant quadrupole–quadrupole interactions in the intermolecular potential.

EXPERIMENTAL

The spectroscopic equipment, sample-handling apparatus and data collecting and processing methods have been described in previous papers.[1,3]

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Table 1. Summary of the pure rotational Raman lines and systems studied

Host gas	Perturbing gases	Pressure range (bar)	Rotational lines studied	Temperature (K)
$^1H_2$	CO, N_2, Ar, He, O_2, HCl	2–100	$S_0(0)$–$S_0(2)$	293
$^2H_2$	CO, N_2, Ar, He, O_2, HCl	2–100	$S_0(0)$–$S_0(4)$	293
$^2H_2$	CO, N_2	2–100	$S_0(0)$	100–293
$^1H_2$	$^1H_2$	1–100	$S_0(0)$–$S_0(2)$	90–293
$^2H_2$	$^2H_2$	1–60	$S_0(0)$–$S_0(4)$	90–375

The systems studied are summarized in Table 1. Sample gases were supplied by the British Oxygen Company with a stated purity of 99.9%. In all the measurements of foreign gas broadening, the partial pressure of the host gas was 1 bar over a total pressure range of 2–100 bar. For the self-broadened $^1H_2$ and $^2H_2$ systems the pressure range was 1–100 and 1–60 bar, respectively. In the case of HCl, used as a perturber, the maximum pressure used was 40 bar. All the spectra were acquired using a Nicolet 1180 data system and calibrated using a thorium emission spectrum from a hollow-cathode lamp. Calibration was carried out immediately following three spectral scans.

Line-width measurements on each rotational line were repeated five times for each pressure. The full width at half maximum intensity (FWHM) was then obtained using a curve analysis program (CAP) described previously.[1] The average of each set of line-width measurements was used in the calculation of the broadening coefficients.

RESULTS

Self-broadening of $^1H_2$ and $^2H_2$

In the pressure region 1–10 bar at 293 K, a narrowing of line width (Dicke narrowing) with increase in pressure was observed for both $^1H_2$ and $^2H_2$. This is shown in Fig. 1 for the $S_0(1)$ rotational line of $^1H_2$. The broadening coefficients, σ cm^{-1} bar^{-1}, for the $S_0(0)$, $S_0(1)$ and $S_0(2)$ lines of $^1H_2$ and the $S_0(0)$–$S_0(4)$ lines of $^2H_2$ are shown in Table 2. The σ values for the $^2H_2$ lines are appreciably larger than those of $^1H_2$. For the $S_0(1)$ line of $^1H_2$ the σ values show an enhancement which has been reported previously.[9] The low intensity of the $S_0(3)$ line and of higher J-value rotational lines of $^1H_2$ prevented further investigation of this effect. The smaller rotational line spacings of $^2H_2$ enabled the $S_0(0)$ to $S_0(4)$ lines to be studied. Enhancement of the σ values for the $S_0(0)$, $S_0(2)$ and $S_0(4)$ lines was observed and this is shown in Fig. 2.

These experimental studies were also repeated at 90 K. To obtain the spectra of the $S_0(2)$ line of $^1H_2$ and the

Table 2. Self-broadening coefficients, σ, for $^1H_2$ and $^2H_2$ at 293 K

$S_0(J)$	$10^3\sigma$ (cm^{-1} bar^{-1}) $^1H_2$	$^2H_2$
0	1.19 ± 0.07	4.05 ± 0.12
1	1.48 ± 0.08	2.69 ± 0.10
2	0.58 ± 0.06	2.46 ± 0.07
3	—	1.22 ± 0.09
4	—	1.14 ● 0.10

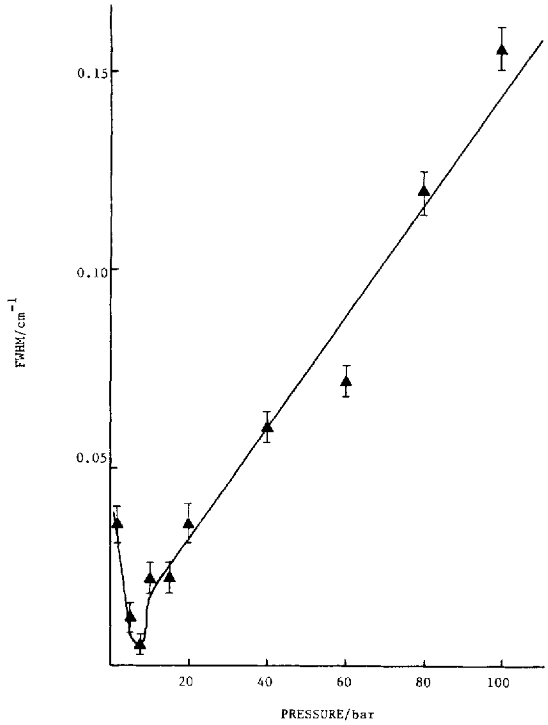

Figure 1. Plot of observed line width against pressure for the $S_0(1)$ line of $^1H_2$ at 293 K.

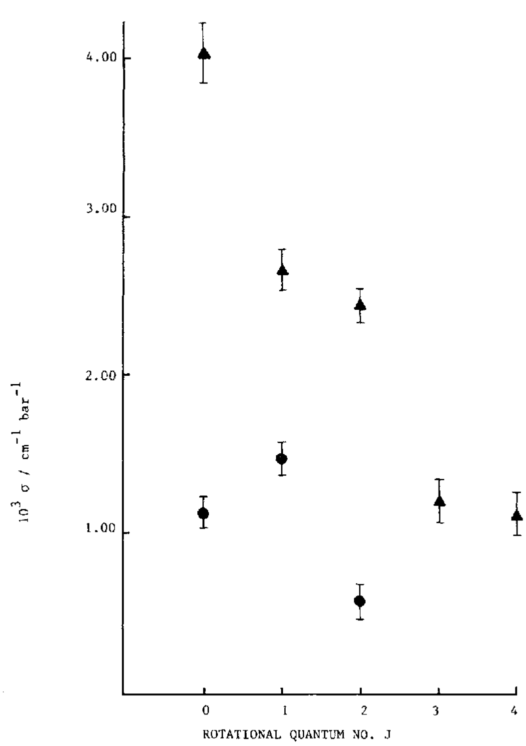

Figure 2. Plot of rotational quantum number, J against the self-broadening coefficient for (●) $^1H_2$ and (▲) $^2H_2$ at room temperature.

$S_0(4)$ line of $^2H_2$ it was necessary to scan the spectrum 16 times. The $S_0(0)$ line of $^2H_2$ was also recorded at temperatures of 200 and 375 K over the pressure range 1–60 bar. The σ values are presented in Table 3 and show that the σ value enhancement observed at 293 K still persists at 90 K.

Foreign gas broadening of $^1H_2$ and $^2H_2$

The broadening coefficients at 293 K for $^1H_2$ and $^2H_2$ perturbed by foreign gases are given in Tables 4 and 5, respectively. The line narrowing observed in the self-broadening studies of $^1H_2$ and $^2H_2$ was also observed here in the region 5–15 bar and examples of this are shown in Fig. 3 for $^1H_2$ perturbed by N_2 and CO at 293 K.

Enhancement of the σ values for the $S_0(1)$ line was observed for $^1H_2$ perturbed by CO, N_2 and HCl but not for $^2H_2$ perturbed by these gases.

The J dependence of the σ values for $^2H_2$ perturbed by He, Ar and O_2 is shown in Fig. 4 and shows that the efficiency of O_2 as a perturber is considerably less than might have been expected from molecular mass considerations. A similar trend has been observed for $^1H_2$ and will be discussed later.

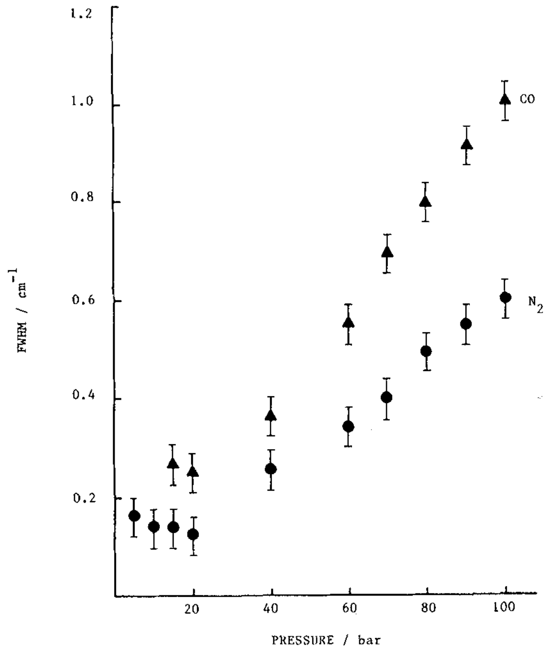

Figure 3. Plot of line width against pressure for the $S_0(1)$ line of $^1H_2$ perturbed by N_2 and CO at 293 K.

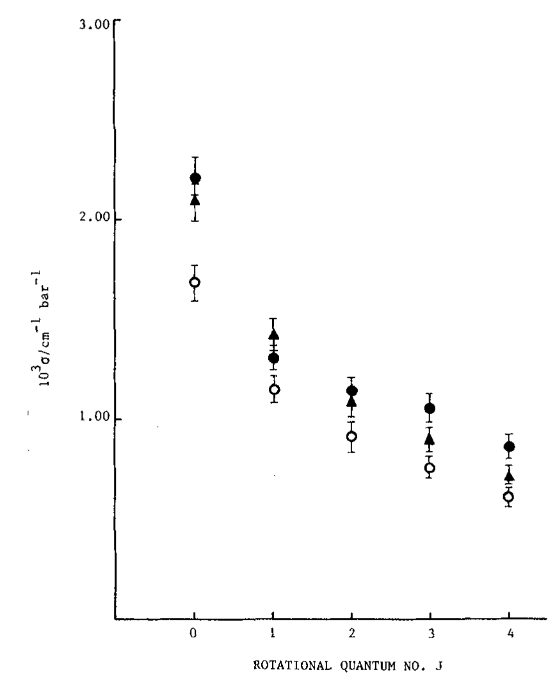

Figure 4. Plot of rotational quantum number, J, against the broadening coefficients of $^2H_2$ perturbed by (●) Ar, (▲) O_2 and (○) He at 293 K.

Table 3. Self-broadening coefficients, σ, for $^1H_2$ at 90 K and $^2H_2$ in the temperature range 90–375 K

	$10^3\sigma$ (cm^{-1} bar^{-1})			
	$^1H_2$	$^2H_2$		
$S_0(J)$	90 K	90 K	200 K	375 K
0	2.33 ± 0.14	8.56 ± 0.26	5.61 ± 0.20	3.34 ± 0.16
1	2.81 ± 0.14	4.83 ± 0.19	—	—
2	1.64 ± 0.15	4.39 ± 0.23	—	—
3	—	2.25 ± 0.11	—	—
4	—	1.93 ± 0.14	—	—

Table 4. Experimental foreign gas broadening coefficients for $^1H_2$ at 293 K

	$10^3\sigma$ (cm^{-1} bar^{-1})		
Perturber	$S_0(0)$	$S_0(1)$	$S_0(2)$
He	1.29 ± 0.07	0.81 ± 0.03	—
Ar	1.59 ± 0.06	1.44 ± 0.04	—
O_2	1.47 ± 0.06	1.41 ± 0.05	—
N_2	6.12 ± 0.3	6.07 ± 0.2	2.8 ± 0.1
CO	7.38 ± 0.4	10.2 ± 0.4	5.23 ± 0.3
HCl	27.6 ± 1.4	32.7 ± 1.8	11.7 ± 0.9

Table 5. Experimental foreign gas broadening coefficients for $^2H_2$ at 293 K

	$10^3\sigma$ (cm^{-1} bar^{-1})				
Perturber	$S_0(0)$	$S_0(1)$	$S_0(2)$	$S_0(3)$	$S_0(4)$
He	1.69 ± 0.08	1.15 ± 0.04	0.92 ± 0.03	0.78 ± 0.03	0.62 ± 0.04
Ar	2.22 ± 0.09	1.31 ± 0.06	1.14 ± 0.05	1.06 ± 0.04	0.87 ± 0.03
O_2	2.10 ± 0.10	1.42 ± 0.08	1.09 ± 0.04	0.89 ± 0.03	0.71 ± 0.05
N_2	10.4 ± 0.6	7.98 ± 0.30	3.69 ± 0.21	2.39 ± 0.24	1.51 ± 0.09
CO	20.0 ± 1.0	13.0 ± 0.5	7.53 ± 0.42	3.75 ± 0.30	2.68 ± 0.31
HCl	136.2 ± 6.8	63.7 ± 2.5	31.8 ± 1.7	17.4 ± 1.0	9.73 ± 0.59

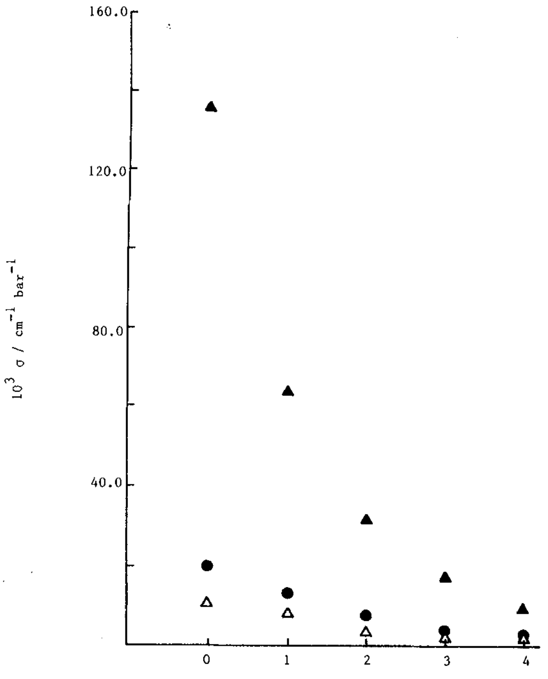

Figure 5. Plot of rotational quantum number, J, against the broadening coefficients of $^2H_2$ perturbed by (△) N_2, (●) CO and (▲) HCl at 293 K.

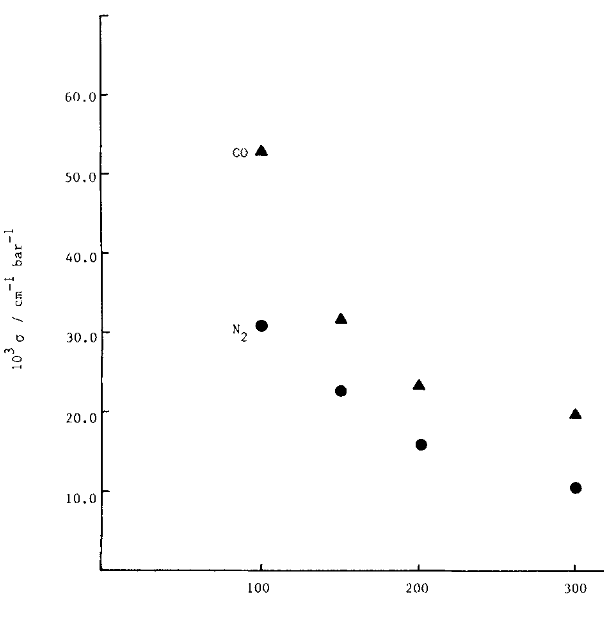

Figure 6. Plot of temperature against the broadening coefficient for the $S_0(0)$ line of $^2H_2$ perturbed by (●) N_2 and (▲) CO.

Table 6. Broadening coefficients, σ, for the $S_0(0)$ line of $^2H_2$ perturbed by N_2 and CO in the temperature range 100–293 K

	$10^3\sigma$ (cm^{-1} bar^{-1})			
Perturber	100 K	150 K	200 K	293 K
N_2	30.6 ± 0.2	22.7 ± 0.2	15.8 ± 0.3	10.4 ± 0.3
CO	52.7 ± 0.2	31.9 ± 0.2	23.3 ± 0.3	20.0 ± 0.3

An increase in σ values of 85% for $^1H_2$ and 100% for $^2H_2$ with CO as the perturber compared with N_2 as the perturber may be attributed to the effect of the small dipole moment (0.11 D) of CO, which is absent in the isoelectronic N_2. The σ values are increased still further when HCl is used as a perturber and this may be ascribed to the larger dipole moment (1.2 D) in HCl. The J dependence of the σ values in $^2H_2$ and the effect of the perturber polarity are shown in Fig. 5 for N_2, CO and HCl.

The effect of temperature on the σ values of the $S_0(0)$ line of $^2H_2$ perturbed by N_2 and CO over the range 100–293 K is shown in Table 6 and Fig. 6. The results are similar to those already observed in a study of the self-broadening of N_2 with temperature.[1] At higher temperatures the σ values tend to a constant value.

DISCUSSION

The σ values for self-broadened $^1H_2$ and $^2H_2$ obtained here are compared with the results of previous studies[4,5,7,10] in Tables 7 and 8. Although the J dependence of the σ values is similar, there is generally little agreement between any of the results. Only the results of Cooper *et al.*[7] and Knaap *et al.*[10] for the $S_0(0)$ and $S_0(1)$ lines of $^1H_2$ are in agreement with each other. The enhancement of σ values for the even J-valued $S_0(J)$ lines in $^2H_2$ and odd J-valued $S_0(J)$ lines in $^1H_2$ has been ascribed to resonant collisions.[9]

The σ values for $^1H_2$ broadened by He and N_2 are compared with those of previous work[4,11] in Table 9. May *et al.*[4] reported that the value of σ for the $S_0(1)$ line

Table 7. Comparison of the room temperature self-broadening coefficients of the pure rotational lines of $^1H_2$ observed in this work with data from previous studies

	$10^3\sigma$ (cm^{-1} bar^{-1})				
$S_0(J)$	This work	Ref. 4	Ref. 5	Ref. 7	Ref. 10
$S_0(0)$	1.19	3.0	0.93	2.8	2.8
$S_0(1)$	1.48	4.6	1.13	3.5	3.5
$S_0(2)$	0.58	—	—	—	2.5
$S_0(3)$	—	—	—	—	2.5
$S_0(4)$	—	—	—	—	1.5

Table 8. Comparison of the room temperature self-broadening coefficients of the pure rotational lines of $^2H_2$ from this work with the data of Knaap *et al.*[10]

	$10^3\sigma$ (cm^{-1} bar^{-1})	
$S_0(J)$	This work	Ref. 10
$S_0(0)$	4.05	5.6
$S_0(1)$	2.69	4.5
$S_0(2)$	2.49	4.1
$S_0(3)$	1.22	3.4
$S_0(4)$	1.14	2.9

Table 9. Comparison of the room temperature foreign gas broadening coefficients of the pure rotational lines of $^1H_2$ observed in this work with data from previous studies

	$10^3\sigma$ (cm^{-1} bar^{-1})			
	This work		Ref. 4	Ref. 11
$S_0(J)$	He	N_2	He	N_2
$S_0(0)$	1.29	6.12	1.80	—
$S_0(1)$	0.81	6.07	2.50	7.0

of $^1H_2$ perturbed by He was enhanced relative to the $S_0(0)$ value, but this was not observed in the present work. Enhancement of the σ values for $S_0(1)$ of $^1H_2$ perturbed by N_2, CO and HCl was observed in the present work and has not been reported previously. In contrast, the σ values for $^2H_4$ perturbed by foreign gases show a classical J dependence.

The σ values for self-broadened $^1H_2$ and $^2H_2$ are much smaller than those observed for N_2, CO and HCl.[1,2] This may be ascribed to the large rotational line spacings and high molecular velocities of $^1H_2$ and $^2H_2$, which lead to large lifetimes and small line widths.

The pure rotational Raman lines of $^1H_2$ and $^2H_2$ perturbed by foreign gases show some interesting trends. Atomic perturbers, such as He and Ar, have only a small effect on the rotational line broadening of $^1H_2$ and $^2H_2$ and a tenfold increase in atomic mass from He to Ar results in an increase of only 30% in the σ values. When N_2 is the perturbing species, a larger change in the σ value as compared with the self-broadened systems is observed. This may be attributed to the presence of a quadrupolar intermolecular potential. CO and N_2 are isoelectronic, have nearly identical molecular masses and have similar magnitudes for their quadrupoles. However, increases in σ values of up to 70% are observed when CO is the perturber instead of N_2. This may be ascribed to the presence of the small dipole moment (0.11 D) in CO.

In the case of HCl as a perturber, there are two reasons for the large increases in σ compared with N_2 and CO. The most important contribution to the increased values must arise from the large dipole moment (1.2 D) of HCl. Of lesser importance is the increase in molecular mass, and hence rotational energy, of HCl over those of N_2 and CO.

An apparent anomaly is observed when O_2 is used as a perturber, namely that the σ values are intermediate between those values given from He and Ar perturbed systems. This is surprising in view of the σ values for self-broadened O_2, which are similar to those of $N_2(1)$. However, it has already been reported[11,12] that in systems for which there is no dipole moment the quadrupole–quadrupole interactions form the dominant part of the intermolecular potential. The small effect of O_2 as a perturber may thus be ascribed to its small quadrupole moment, namely -1.2×10^{-36}C compared with -4.7×10^{-36}C for N_2.

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