LINESTRENGTHS IN THE 3-0 VIBRATION-ROTATIONAL BAND OF GASEOUS ¹H³⁵Cl AND THE ELECTRIC DIPOLE MOMENT FUNCTION

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Linestrengths in the 3-0 band of ¹H³⁵Cl and ¹H³⁷Cl have been remeasured. The mean value obtained for the pure vibrational transition matrix element $\langle 0|M(R)|3\rangle$ of ¹HCl is + (1.875±0.024)×10⁻³³ C m. Based on this value, a value of $\langle 0|M(R)|2\rangle$ from Boulet et al. which is confirmed, and other published data, a new determination of the electric dipole moment function of HCl has been made in both the M(x) and M(z) representations.

1. Introduction

The radial function describing the dependence of the electric dipole moment of a diatomic molecule on the internuclear separation R is important for both theoretical and experimental applications. Theoretically, it may be used to test the accuracy of quantum computations, because for this purpose the dipole moment function is more sensitive than the total energy to the quality of the wavefunctions [1]. Experimentally this function is taken to determine the intensity of all vibration-rotational transitions involving one photon, within a particular electronic state, according to either absorption or emission experiments. Indeed the intensities of such absorption transitions in the infrared spectral region are the primary source of experimental data according to which this function can be determined [2].

In the case of HCl the intensities of individual lines in the fundamental vibration-rotational band have recently been remeasured with great precision [3]. Likewise for the overtone transitions from the ground vibrational state v=0 to excited states with $4 \le v' \le 7$ that occur in the near-infrared and visible regions, the linestrengths have been reasonably accurately determined, despite the weakness of these transitions [4]. However for the 3-0 band in the near-infrared, the only measurements of individual lines were carried out many years ago [5], at a time when instrumentation was not nearly so advanced as for the more recent experiments. Furthermore the concurrent measurements [5] of the linestrengths of the fundamental band produced values significantly smaller than those recently remeasured [3]. In addition, the estimate [6] of the bandstrength by the method of pressure broadening produced a result much larger than that [5] from the sum of the linestrengths. Because of the importance of the value of this bandstrength in determining the dipole moment function, we have remeasured the linestrengths of this 3-0 band at high resolution so as to separate the individual lines, followed by analysis of the spectrum by means of interactive computer graphics. Our results are presented herein.

We have also remeasured the linestrengths of the 2–0 band of HCl, but in this case our results are consistent with the results of Boulet et al. [7] which were

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in turn consistent with some earlier results, although not with the commonly preferred value [8] of the bandstrength (or rather the pure vibrational matrix element to which it is equivalent). However, the latter value was really a weighted mean, biased in favour of the results of Benedict et al. [5], of some earlier results which are now found to be consistent with neither the results of Boulet et al. [7] nor our own new measurements. Therefore we have determined a new dipole moment function for HCl based on the best available data, according to a statistically weighted fit of the consistent data from both intensities of vibration-rotational bands and expectation values from the Stark effect in measurements at radio frequencies [9].

2. Experiments

HCl gas (Matheson, 99.5% purity) was admitted to a standard gas cell having a length 0.1000 ± 0.0005 m of absorbing path enclosed with KCl windows for the 3–0 band, or a specially constructed cell of length 0.0094 ± 0.0004 m enclosed with thin windows of fused silica for the 2–0 band, on a high-vacuum manifold according to standard techniques. Pressures in the range $0.5 \times 10^5 \le P \le 1.0 \times 10^5$ N m⁻² were measured by means of a capacitance manometer (MKS Baratron) with an accuracy ± 50 N m⁻². During spectral measurements on a Bomem DA3.002



Fig. 1. Plot of linear absorbance versus wavenumber for the 3–0 vibration-rotational band of gaseous HCl in a length 0.100 m of absorbing path at 100027 N m⁻² and 298.15 K. The net absorbance of the most intense lines is ≈ 0.05 in units of $\ln[I_0(\nu)/I(\nu)]$, and the uneven baseline is an instrumental artefact.

interferometric spectrometer with SiO₂ beamsplitter and InSb detector cooled by liquid N₂, the temperature of the gas cell was monitored by a digital thermocouple on its enclosure and found to be constant within ± 0.2 K during the several hours of each experiment. The spectral resolution was set at 5.0 m⁻¹ for the 3–0 band or 3.2 m⁻¹ for the 2–0 band, much smaller than the measured linewidths, and the accuracy of the absorption maxima was also limited by the linewidth to ± 0.5 m⁻¹. The spectra were analysed interactively using programs supplied with the spectrometer. The spectrum of the 3–0 band is shown in fig. 1.

3. Results of intensity measurements

The measured wavenumbers at maximum absorption, strengths, and full widths $v_{1/2}$ at half maximum intensity of the lines in the 3-0 bands of ¹H³⁵Cl are listed in table 1; the corresponding data of ¹H³⁷Cl are consistent with these results, but are of lesser accuracy due to the smaller intensities resulting from the smaller relative abundance of the ³⁷Cl isotope. In order to ensure that there was a complete absence of saturation of absorption at any line centre, with consequent deviation from the Lambert law of exponential attenuation, a relatively small length of absorbing path was used, with adequate pressure to provide collisional broadening of the lines to a width much larger than the effective spectral resolution. Because these conditions to prevent saturation were achieved with relatively small pressures, the maximum absorbance of the less intense lines was not large by comparison with the noise amplitude. For this reason the measurements of the integrated intensities of some lines due to ¹H³⁷Cl were similarly difficult and consequently inaccurate.

The intrinsic molecular linestrengths S were calculated by means of the equation

$$S = \frac{1}{Nb} \int \ln\left(\frac{I_0(\nu)}{I(\nu)}\right) d\nu$$

in which I_0 and I are respectively incident and transmitted intensity at wavenumber ν through the sample in an absorbing path of length b, ln is the natural logarithm, and N is the concentration of the particular isotopic species as a number density (molecules Table 1

$\frac{\mathbf{P}(J)}{(\mathbf{m}^{-1})}$	$\frac{\nu_{1/2}}{(m^{-1})}$	<i>S</i> (10 ⁻²⁵ m)		J	R(J)	$v_{1/2}$	\$ (10 ⁻²⁵ m)	
		obs.	calc.		(m)	(m ⁻ .)	obs.	calc.
				0	836584.41	42	5.27	5.51
832592.7	44	5.02	4.83	1	838309.01	44	10.04	10.62
830322.88	46	7.79	7.80	2	839850.60	44	13.33	12.60
827878.46	48	8.85	8.53	3	841204.46	43	12.23	12.62
825254.76	46	7.86	7.51	4	842377.85	39	12.35	10.72
822451.07	41	6.18	5.61	5	843361,95	34	9.35	7.92
819480.49	35	3.41	3.64	6	844156.02 ^{a)}			5.14
816336.83	28	2.34	2.08	7	844763.48	26	3.14	2.96
813017.5		1.44	1.06	8	845182.72	25	1.73	1.52
809529.4			0.48	9	845406.84		0.57	0.70
				10	845446.3		0.25	0.29
				11	845289.7		0.14	0.11

^{a)} R(6) line of ¹H³⁵Cl and R(7) line of ¹H³⁷Cl are incompletely resolved.

per unit volume); no corrections for the deviations from the ideal gas law or for beam convergence were made. The numerical evaluation of the integrals was made over a range of up to two (average) linewidths on either side of the wavenumber of maximum absorption of a particular line, or until the extent of the absorption was indistinguishable from the noise level. The proportions of ³⁵Cl and ³⁷Cl were assumed to be those of average natural abundance [3].

The bandstrength may be estimated as the sum of the linestrengths, thus $(1.10\pm0.04)\times10^{-24}$ m, being a weighted mean of all the data for ¹H³⁵Cl and ¹H³⁷Cl. The inclusion of data of both isotopic variants in this mean is justified by the more accurate results for the 1-0 band in which no significant difference could be detected for these isotopic species. This value may be compared with the previous values (in the same SI units) 0.94×10^{-24} [5] and 1.50×10^{-24} m [6]. The strengths of the individual lines in the band of ¹H³⁵Cl are listed in table 1; based on the reproducibility in experiments with different densities of sample in the same cell, the relative accuracy of these values for the more intense lines is estimated to be about 8%. No significant dependence of linestrength on pressure of sample could be detected within the range of densities tested. The widths $\nu_{1/2}$ of the lines were also measured. Because the R(6) line of ¹H³⁵Cl is incompletely separated from the R(7) line of ¹H³⁷Cl, no meaningful value of either linewidth or linestrength could be directly measured. Listed also

in table 1, the values of $\nu_{1/2}$, having a relative accuracy estimated about 5%, are the full widths at half maximum absorbance for a sample at 100027 N m^{-2} and 298.15 K. These widths were found to be roughly linearly proportional to pressure within the range of densities tested, and were thus much larger than either the effective resolution ($\approx 5.0 \text{ m}^{-1}$) of the spectrometer or the Doppler width which is calculated to be ≈ 1.72 m⁻¹ in this 3–0 band. That the measured widths are approximately linearly proportional to the pressure is consistent with the mechanism for broadening being collisions between HCl molecules. The widths generally decrease as the rotational quantum number J increases, in accordance with earlier results [5], but there may be evidence for maximum values at P(3) and R(2) in their respective branches. Because of the only moderate ratio of maximum absorbance to noise amplitude, no attempt was made to fit the lines to shape functions; for this reason any conclusions from the measured linewidths must be both qualitative and tentative. Any shift of the wavenumber of maximum absorbance of the lines from the wavenumbers reported [10] at small densities is much smaller than the linewidths, and therefore not measurable in the present experiments.

4. Dipole moment function

The linestrengths S in the different experiments, for both ${}^{1}\text{H}{}^{35}\text{Cl}$ and ${}^{1}\text{H}{}^{37}\text{Cl}$, were converted to the squares of the corresponding vibration-rotational matrix elements, $|\langle vJ|M(R)|v'J'\rangle|^{2}$, of the operator M(R) for the electric dipole moment function of the internuclear distance for the transition from the vibration-rotational state $\langle vJ|$ of smaller energy to the final state $|v'J'\rangle$ according to the relation

$$S = \frac{8\pi^3}{3hc} \frac{\exp(-hcE_{\nu J}/k_{\rm B}T)}{4\pi\epsilon_0 Q} \nu_0$$
$$\times [1 - \exp(-hc\nu_0/k_{\rm B}T)]$$
$$\times |\iota| |\langle \nu J|M(R)|\nu'J'\rangle|^2.$$

In this equation Q is the rotational partition function, ν_0 is the wavenumber at maximum absorbance of the line to which the strength pertains at temperature T, $i \equiv \frac{1}{2} [J'(J'+1) - J(J+1)]$ is a running number, E_{uJ} is the energy of the lower state of the transition expressed conventionally in wavenumber units, and the other symbols represent the universal mathematical and physical constants. Then the values, weighted according to the squares of the corresponding linestrengths, of these matrix elements were fitted as a polynomial function of i to determine the squared pure vibrational matrix element $|\langle v|M(R)|v'\rangle|^2$ as the intercept on the ordinate axis:

$$\begin{split} |\langle vJ|M(R)|v'J'\rangle|^2 \\ &= |\langle v|M(R)|v'\rangle|^2(1+C_v^{\nu'}\iota+D_v^{\nu'}\iota^2+\dots) \;. \end{split}$$

The magnitude of the square root of the weighted mean of these intercepts for ${}^{1}\text{H}{}^{35}\text{Cl}$ and ${}^{1}\text{H}{}^{37}\text{Cl}$ at different pressures is $(1.875\pm0.024)\times10^{-33}$ C m. According to the same fit, the value of the coefficient C_{0}^{3} in the Herman-Wallis factor was found to have a positive sign, and only this positive sign, not the rough value, was used to resolve the ambiguity of the sign of the experimental matrix element, according to the procedure previously described in detail [2]. It should be noted that, although the value of C_{0}^{3} was only roughly determined by means of the fit of the vibration-rotational matrix elements as a function of *t*, because of both the limited accuracy and limited extent of the data which collectively affect severely the accuracy of the small correction terms in the Herman-Wallis factor, the ordinate intercept was much better defined.

The latter value was added to a previously collected set [11] of all the vibrational matrix elements reported for ¹H³⁵Cl and ²H³⁵Cl. At the same time, the weights of all values of these elements due to Benedict et al. [5] were adjusted so as to eliminate from the resulting fit any sensitivity to their values. Then the most precise remaining value for the $\langle 0|M(R)|2 \rangle$ element is $-(2.712\pm0.030)\times10^{-32}$ C m due to Boulet et al. [7], whose result is confirmed by our measurements. For use in the fitting process, the dipole moment function M(R) may be expressed more conveniently as M(x),

$$M(x) = \sum_{j=0}^{7} M_j x^j$$

in terms of the reduced variable $x \equiv (R - R_e)/R_e$ for internuclear displacement from equilibrium. Thus was made a grand fit of all the thirty-four experimental values of the matrix elements by means of a weighted multiple linear regression program [11] according to the overdetermined system of eight linear equations [2]

$$\langle v | M(x) | v' \rangle = \sum_{j=0}^{7} M_j \langle v | x^j | v' \rangle$$

in which $\langle v | x^j | v' \rangle$ are the matrix elements of x to various powers for which analytic expressions are available [12], based on the values of the potential energy coefficients a_j previously reported [13]. The values of the corresponding coefficients M_j are listed in table 2. The analogous alternative representation M(z),

Table 2 Values of coefficients M_j and P_j in the electric dipole moment functions M(x) and M(z) respectively

j	$M_j (10^{-30} \mathrm{Cm})$	$P_j (10^{-30} \mathrm{Cm})$			
0	3.645867±0.000253	3.645867±0.000253			
1	4.12334 ±0.00147	4.12334 ±0.00147			
2	0.06882 ± 0.0177	2.13049 ±0.0177			
3	-5.1096 ± 0.0438	-4.00995 ± 0.0478			
4	-3.0648 ± 0.088	-10.1621 ± 0.114			
5	-1.174 ± 0.142	-14.676 ± 0.230			
6	-1.457 ± 0.242	-18.290 ± 0.478			
7	1.172 ±0.69	-19.98 ±1.17			

$$M(z) = \sum_{j=0}^{7} P_j z^j$$

in terms of the superior variable [14] $z \equiv 2(R-R_e)/(R+R_e)$ that is well behaved in the approach to both the limits of the united atom and the separate atoms, however embodies the advantage [15] that it may be extended to approach smoothly those limits; the values of the coefficients P_j are also presented in table 2.

On the basis of this dipole moment function for ${}^{1}\text{H}{}^{35}\text{Cl}$, the linestrengths for the 3–0 band were calculated. These calculated and observed values may be compared in table 1.

5. Discussion and conclusions

The present measurements of the strengths of the lines in the 3–0 vibration-rotational band of ¹H³⁵Cl have enabled a new determination of the electric dipole moment matrix element $\langle 0|M(R)|3 \rangle$. The value is $+(1.875\pm0.024)\times10^{-30}$ C m the sign of which has been determined indirectly [2] by means of the positive sign of the Herman-Wallis coefficient C_0^3 . Although the nominal error (one standard error, by means of standard statistical methods) is appended to this value, it should probably be considered to be a lower limit to the true accuracy for reasons previously discussed [3]. The value of the corresponding bandstrength is intermediate between the two previously published values [5,6], but differs significantly from them.

The combination of this value and other published values of vibrational matrix elements has enabled the new determination of the electric dipole moment function M(R) of HCl, according to the polynomial representations M(x) and M(z) of which the coefficients are listed in table 2. Because the function was assumed to have no dependence on nuclear mass, according to the Born-Oppenheimer approximation, the resulting function applies equally well to any isotopic variant of HCl, and indeed some values of experimental expectation values [9] of ²H³⁵Cl were included in the fitting process. The reasonable agreement between the measured and calculated linestrengths in table 1 confirms that this function applies well to the 3-0 band, and in fact calculations of the linestrengths of the other bands also provide

very satisfactory agreement with experimental values.

While the present experiments were in progress, there appeared a report [16] of a new measurement of the strength of the P(3) line within the 3–0 band of $^{1}H^{35}Cl$ which led to a value 18% greater than that specified by Benedict et al. [5], but which is entirely consistent with the present values. Thus there seems to be a systematic error, to the extent of about 20%, in the experimental values of the linestrengths, and correspondingly the bandstrengths, reported by Benedict et al. [5], by comparison with more recent measurements; it seems advisable to regard with caution the remaining values not yet remeasured, and perhaps to expect that they may be considered to represent lower limits of the true values, similarly too small by about 20%.

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