# Molecular $GaH_2Cl$: Matrix Infrared Spectrum and *ab initio* Investigations†

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On the basis of the matrix IR spectrum of molecular $GaH_2Cl$, formed in a matrix reaction of $H_2$ and molecular GaCl, the force constants of the Ga–Cl and Ga–H bonds have been determined to be 2.38 and 2.26 mdyn $Å^{-1}$ respectively; these results are confirmed by *ab initio* MP2 calculations.

Recently we reported the characterisation of matrix-isolated dichlorogallane, $GaHCl_2$, obtained after a photolytic activation of the high-temperature molecule GaCl and HCl under matrix conditions.[1] To extend knowledge of elusive gallium compounds with co-ordination number three we investigated the formation and bonding of matrix-isolated $GaH_2Cl$. This molecule is of additional interest, since the structure of its chloro-bridged dimer $(H_2GaCl)_2$[2] has recently been determined by means of electron diffraction and *ab initio* calculations.[3,4]

The formation of monomeric $GaH_2Cl$ after photolysis of GaCl and $H_2$ in solid argon develops in the following way.‡ After cocondensation of GaCl and $H_2$ with an excess of argon (about 1:4:200) the IR spectrum showed absorptions due to GaCl (343 $cm^{-1}$) and $(GaCl)_2$ (221 and 209 $cm^{-1}$).[6] The peaks assigned to mono- and di-meric GaCl decreased after 10 min of photolysis with the entire spectrum of the mercury lamp. New absorptions were detected at 1978.1, 1964.6, 731.4, 620.0, 510.1 and 406.9 $cm^{-1}$ (Fig. 1). In different experiments the IR spectra showed equal intensity ratios for all these absorptions and therefore they have to be attributed to one species only.§ The vibrational spectra of photolysed mixtures of GaCl and $D_2$ or HD isolated in solid Ar gave evidence for the formation of a molecule containing two equivalent hydrogen atoms (Table 1). The absorptions at 1978.1 and 1964.6 $cm^{-1}$ are assigned to the antisymmetric and symmetric stretching vibrations of the $GaH_2$ group. This assignment is plausible by comparison with the GaH stretching mode of $GaHCl_2$ at 2015.3 $cm^{-1}$.[1] The absorption at 406.9 $cm^{-1}$ is attributed to the Ga–Cl mode because of its energy and its gallium and chlorine isotopic splitting pattern ($^{69}GaH_2{}^{35}Cl$, 406.91; $^{71}GaH_2{}^{35}Cl$, 404.98; $^{69}GaH_2{}^{37}Cl$, 399.20; $^{71}GaH_2{}^{37}Cl$, 397.27 $cm^{-1}$). The corresponding stretching vibrations of $GaHCl_2$ occur at 437.3 and 414.3 $cm^{-1}$.[1] The assignment of the remaining three bands at 731.4, 620.0 and 510.1 $cm^{-1}$ can be made by means of normal coordinate analyses for the isotopomers $GaH_2Cl$, GaH(D)Cl and $GaD_2Cl$.¶

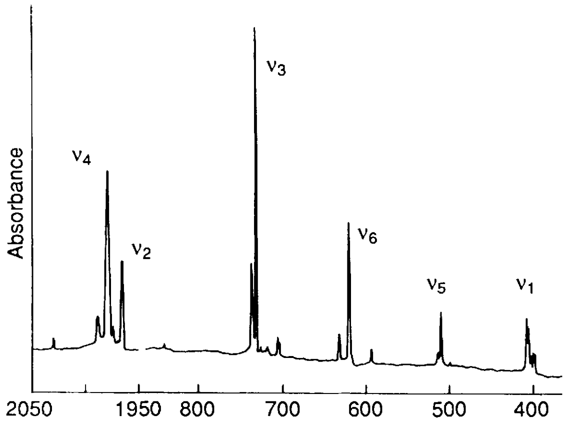

**Fig. 1** Argon-matrix IR spectrum after the condensation of GaCl and $H_2$ and subsequent photolysis

For the molecule $GaH_2Cl$ ($C_{2v}$ symmetry) we expect six normal modes belonging to three irreducible representations $A_1$ $\nu_1[\nu(GaCl)]$, $\nu_2[\nu_{sym}(GaH_2)]$, $\nu_3[\delta(GaH_2)]$; $B_1$ $\nu_4[\nu_{asym}(GaH_2)]$, $\nu_5[\rho(Cl)]$; and $B_2$ $\nu_6[\gamma]$. The results of the normal coordinate analyses presented in Table 1 are based on structural data determined with the aid of an *ab initio* MP2 calculation (*cf.* Table 2). For the $B_1$ representation the force constants ($F_{44}$, $F_{45}$, $F_{55}$) (mdyn $Å^{-1}$, normalised to the Ga–H distance) are obtained on the grounds of a simple valence force field ($F_{45} = 0$). Based on these force constants there is a good agreement between the calculated and experimental bands of $GaD_2Cl$ (calc. 1415.7, 371.4; exptl. 1430.5, 371.2 $cm^{-1}$) (Table 1). The three vibrational modes of $GaH_2Cl$ in the $A_1$ representation are best reproduced by a general valence force field. Within these calculations the band at $\nu_3$ 731.4 $cm^{-1}$ is assigned to the $GaH_2$ deformation mode. The frequencies of GaH(D)Cl obtained experimentally ($C_s$ symmetry) are confirmed, if the force constants of the $A_1$ and $B_1$ representations (calculated from the frequencies of $GaH_2Cl$ and $GaD_2Cl$) are transformed to a single force-constant matrix of A′ symmetry. The fundamentals $\nu_1$ and $\nu_5$ of GaH(D)Cl show strong coupling.‖

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† *Non-SI units employed:* dyn = $10^{-5}$ N, au ≈ 4.36 × $10^{-18}$ J.

‡ A high-temperature gas of GaCl is obtained when $Cl_2$ is passed at 1170 K over liquid gallium.[1] Photolysis was performed with a high-pressure mercury lamp; IR spectra being recorded with a Bruker IFS 66v FTIR spectrometer. Other experimental details have been described earlier.[5]

§ Besides the band at 406.9 $cm^{-1}$ each of the new absorptions exhibits a blue-shifted satellite band of lower intensity which is tentatively assigned to matrix shift effects (1987.3, 1973.3, 736.3, 631.6 and 513.0 $cm^{-1}$; large hydrogen displacements are involved in these normal vibrations).

¶ However small discrepancies between experimental and calculated H/D isotopic shifts have to be expected since differences in anharmonicity for the GaH modes between the isotopomeric species are large and unknown.

‖ Since the potential energy distribution, $\nu_1\{77\%$ [$\nu$(GaCl)], 25% $\rho$(Cl)$\}$, $\nu_5\{28\%$ [$\nu$(GaCl)], 65% $\rho$(Cl)$\}$, exhibits strong mixing of $S_1$ and $S_5$ in both normal modes ($\nu_1$ and $\nu_5$) and since only a single absorption is observed, an unambiguous assignment does not seem possible. However, the calculated value of 408.5 $cm^{-1}$ for $\nu_1$ is very close to the observed absorption at 409.8 $cm^{-1}$ and therefore the latter should also have predominantly $S_1$ character. Obviously there is an intensity borrowing between $\nu_1$ and $\nu_5$, resulting in a strong absorption at 409.8 $cm^{-1}$ and a weak one (not detectable in our experiment) which should be located close to the predicted fundamental at 398.7 $cm^{-1}$.

**Table 1** Vibrational bands (cm$^{-1}$) of $GaH_2Cl$, $GaD_2Cl$ and GaH(D)Cl observed in argon-matrix experiments and calculated by normal coordinate analysis (n.c.a.) and the MP2 *ab initio* method. Infrared intensities in km mol$^{-1}$, MP2 force-constant matrix (mdyn Å$^{-1}$), normalised to the Ga–H distance

| | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ |
|---|---|---|---|---|---|---|
| $^{69}GaH_2{}^{35}Cl$ | | | | | | |
| exptl. | 406.91 | 1964.64 | 731.38 | 1978.14 | 510.08 | 620.01 |
| n.c.a. | 406.91 | 1964.64 | 731.38 | 1978.14 | 510.08 | 620.01 |
| MP2 | 415 (72) | 2098 (57) | 771 (196) | 2105 (183) | 519 (38) | 650 (120) |
| $^{69}GaD_2{}^{35}Cl$ | | | | | | |
| exptl. | 406.43 | 1408.27 | 523.60 | 1430.45 | 371.23 | 448.86 |
| n.c.a. | 406.30 | 1392.54 | 521.97 | 1415.74 | 371.39 | 449.72 |
| MP2 | 415 (73) | 1487 (32) | 550 (97) | 1506 (98) | 378 (22) | 472 (66) |
| $^{69}GaH(D)^{35}Cl$ | | | | | | |
| exptl. | 409.80 | 1971.88 | 660.99 | 1419.36 | * | 544.32 |
| n.c.a. | 408.52 | 1965.69 | 655.28 | 1404.33 | 398.68 | 541.60 |

Symmetry coordinates [$R = r$(Ga–Cl), $r = r$(Ga–H), $\alpha$ = H–Ga–Cl, $\beta$ = H–Ga–H]: $A_1$ $S_1 = R$, $S_2 = 2^{-\frac{1}{2}}(\Delta r_1 + \Delta r_2)$, $S_3 = 6^{-\frac{1}{2}}(-\Delta\alpha_1 - \Delta\alpha_2 + \Delta\beta)$; $B_1$ $S_4 = 2^{-\frac{1}{2}}(\Delta r_1 - \Delta r_2)$, $S_5 = 2^{-\frac{1}{2}}(\Delta\alpha_1 - \Delta\alpha_2)$; $B_2$ $S_6 = \gamma$. Force-constant matrix resulting from n.c.a. (*a*) and MP2 calculation (*b*): (*a*) $F_{11} = 2.38 \pm 0.02$, $F_{12} = 0.15 \pm 0.15$, $F_{13} = -0.1$, $F_{22} = 2.25 \pm 0.03$, $F_{23} = 0.1 \pm 0.1$, $F_{33} = 0.11 \pm 0.01$, $F_{44} = 2.269$, $F_{55} = 0.145$, $F_{66} = 0.0764$; (*b*) $F_{11} = 2.433$, $F_{12} = 0.073$, $F_{13} = -0.093$, $F_{22} = 2.598$, $F_{23} = 0.053$, $F_{33} = 0.117$, $F_{44} = 2.269$, $F_{45} = 0.041$, $F_{55} = 0.150$, $F_{66} = 0.084$.
* See text.

**Table 2** The MP2 optimised geometries (pm, °), energies (au) and results of the Roby–Davidson population analyses (π-SEN in parentheses, Q = net atomic charge)

| | GaH | GaCl | $GaH_3$ | $GaH_2Cl$ | $GaHCl_2$ | $GaCl_3$ |
|---|---|---|---|---|---|---|
| Symmetry | $C_{\infty v}$ | $C_{\infty v}$ | $D_{3h}$ | $C_{2v}$ | $C_{2v}$ | $D_{3h}$ |
| $E_{tot}^{MP2}$ | −1922.480 975 | −2381.764 348 | −1923.673 540 | −2382.924 845 | −2842.170 280 | −3301.409 191 |
| $r$(Ga–H) | 164.9 | | 154.9 | 153.6 | 152.7 | |
| $r$(Ga–Cl) | | 223.5 | | 216.9 | 214.4 | 212.5 |
| H–Ga–H | | | 120 | 130.3 | | |
| Cl–Ga–Cl | | | | | 115.3 | 120 |
| SEN(GaCl) | | 1.29 (0.46) | | 1.33 (0.26) | 1.26 (0.17) | 1.24 (0.13) |
| SEN(GaH) | 1.36 | | 1.47 | 1.44 | 1.40 | |
| $Q$(Ga) | 0.17 | 0.26 | 0.26 | 0.35 | 0.52 | 0.69 |
| $Q$(Cl) | | −0.26 | | −0.21 | −0.23 | −0.23 |
| $Q$(H) | −0.17 | | −0.09 | −0.07 | −0.06 | |

In any case the out-of-plane mode $\nu_6$ belongs to a separate representation ($B_2$ or A″). By means of the force constant $F_{66}$ the assignments for $\nu_6$ of $GaH_2Cl$, GaH(D)Cl and $GaD_2Cl$ are confirmed. The geometric structure based on the *ab initio* MP2 calculation is in agreement with these experimental data, since the *G* matrix for the out-of-plane mode contains all structural elements (distances and angles) of the $GaH_2Cl$ molecule. The stretching force constants expressed in internal coordinates are $f$(GaCl) = 2.38 and $f$(GaH) = 2.26 mdyn Å$^{-1}$.

In addition to spectroscopic experiments $GaH_2Cl$ was examined by means of MP2 *ab initio* calculations. The findings confirm the experimental results (geometry used in normal coordinate analysis, IR frequencies and their assignments and the force-constant matrix). The basis sets[7] used are of DZP quality or better.† We tested their quality by calculating bond distances and vibrational frequencies for the GaH and GaCl molecules. Since these parameters for both species calculated at the MP2 level agree best with the experimental ones, only results of calculations including electron correlation are reported for the gallanes under discussion.‡ Table 2 shows the *ab initio* MP2 results for the $GaCl_3$ molecule, the recently synthesised species $GaHCl_2$,[1] $GaH_2Cl$,§ the still hypothetical gallane $GaH_3$ and for comparison the monovalent gallium compounds GaCl and GaH. The ground state of the molecules is determined to be of $D_{3h}$ ($GaH_3$, $GaCl_3$) and $C_{2v}$ symmetry ($GaH_2Cl$, $GaHCl_2$) respectively. In accordance with chemical intuition the Ga–H bond distance decreases from $GaH_3$ to $GaHCl_2$ whereas the Ga–Cl bond shows a similar tendency on going from $GaH_2Cl$ to $GaCl_3$. Oxidation of the monovalent species GaH and GaCl to the molecules containing trivalent gallium causes a strong decrease in bond distances.

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† H (5s1p)/[3s1p] η(p) = 1.0, Cl (12s9p2d)/[7s5p2d] η(d) = 1.30 and 0.29, and Ga (12s9p5d)/[6s5p3d] η(d) = 0.23. The calculations are performed using the CADPAC (MP2 geometry optimisations)[8] and TURBOMOLE (Roby–Davidson population analyses)[9,10] program packages.

‡ After reoptimisation of the chlorine and gallium basis sets[11] for the GaCl molecule we calculate for this species [self-consistent field (SCF) level] a bond distance of 224.6 pm. A geometry optimisation using these basis sets at the MP2 level results in a distance of 223.5 pm for GaCl which demonstrates the important influence of electron correlation (experimental value 220.4 pm[12]). For GaH we calculate a distance of 166.6 pm at the SCF level and 164.9 pm on the basis of MP2 theory (experimental 166.2 pm[12]). Furthermore the vibrational frequencies for GaCl and GaH determined at the MP2 level are in good accord with the experimental ones [GaH MP2, 1692 cm$^{-1}$ (intensity 805 km mol$^{-1}$), exptl. $\omega_e$ 1604.52 cm$^{-1}$ [12] GaCl MP2, 363 cm$^{-1}$ (intensity 102 km mol$^{-1}$), exptl. $\omega_e$ 365.3 cm$^{-1}$ [12]].

§ Our theoretical investigations confirm Lammertsma and Leszczynski's results[3] for the reaction energy of $GaCl + H_2 \longrightarrow GaH_2Cl$ to be about zero (−2 kJ mol$^{-1}$) [$E_{tot}(H_2) = -1.159\,851$ au].

Considering some typical deviations* between calculated and measured frequencies, our assignment of the matrix spectra of $GaH_2Cl$ is strongly confirmed by the MP2 frequencies (Table 2). Furthermore the force-constant matrices deduced from the *ab initio* calculations fit in with those force constants deduced from the experimental frequencies. This is especially valid for the interaction force constants.

A further insight into chemical bonding of $GaH_2Cl$ is obtained by Roby–Davidson population analyses[9,10] (Table 2).† As expected the atomic charge at gallium increases in the sequence $GaH_3$ to $GaCl_3$. The SENs of the Ga–H and Ga–Cl bonds indicate single bonding, which is slightly strengthened by $\pi$-back bonding for the Ga–Cl bonds.

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* Frequencies obtained from MP2 calculations are normally 5% higher than $\omega_e$ values obtained experimentally. Since both frequencies refer to the harmonic potential, the shifts between the observed, anharmonic frequencies and the calculated (MP2) ones are even larger especially if vibrations with large amplitudes like GaH are involved.

† The shared electron number (SEN)[10] provides a reliable measure of the covalent bond strength. Typical SEN values are: $\sigma$ bonds (C–C, C–H) 1.4, double bonds (C=C) 2.2, triple bonds (C≡C, $N_2$) 3.3. A reduced SEN is found for polar bonds such as in NaF (0.3) and for weak bonds such as in $Cl_2$ (0.9) or $F_2$ (0.6).[9]

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