Characterization of Isolated Ga_2 Molecules by Resonance Raman Spectroscopy and Variations of Ga–Ga Bonding

Hans-Jörg Himmel* and Benjamin Gaertner[a]

Abstract: Isolated Ga_2 dimers were characterized in an argon matrix with the aid of resonance Raman and UV/Vis spectroscopy. The resonance Raman spectra gave evidence of not only the ν(Ga–Ga) fundamental, but also four overtones. Each of the signals exhibits $^{69}Ga/^{71}Ga$ isotopic splitting leading to the triplet pattern characteristic of two equivalent Ga atoms. On the basis of the experimental data, a harmonic frequency and anharmonicity constant have been determined for Ga_2. An estimate of the dissociation energy on the assumption of a Morse-type potential energy curve results in a D_e value (upper limit) of about 145 kJ mol^{-1}. The force constant (64.8 ± 0.3 N m^{-1}) and dissociation energy of Ga_2 are compared with those of other diatomics and those of molecules featuring Ga–Ga bonds.

Keywords: gallium · matrix isolation · metal atom dimers · resonance Raman spectroscopy

Introduction

There is something special about the Ga–Ga bond. In solid α-Ga metal, for example, Ga_2 pairs seem to be present, and the shortest Ga–Ga distances are 248.2 pm.[1,2] On this basis, the α-Ga modification has been described as a "molecular structure" with Ga_2 dumbbells as covalently bonded central molecular units.[2] It has been argued by von Schnering and Nesper, however, that there is more "quasi-localized" bonding in the structure, and that α-Ga can also be understood as an inorganic polymer.[1] As a consequence of the presence of the Ga_2 dumbbells, the Raman spectrum of solid gallium shows a strong signal at 246 cm^{-1} which was assigned to the symmetric a_g combination of the stretching vibrations from two Ga_2 units.[3] There is some indication of the coexistence of monoatomic and diatomic molecular fluid character in liquid gallium.[4] A Ga_2 unit (Ga–Ga 233 pm) was also found in the center of the metalloid cluster compound $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$.[5] All these results show that Ga_2 is an important building block, and have stimulated interest in the properties exhibited by a direct Ga–Ga bond.

Several molecules featuring a direct Ga–Ga bond are now known, and examples include molecules with a Ga–Ga single bond. Thus, the $[Ga_2Cl_6]^{2-}$ ions in $Li_2[Ga_2Cl_6]$[6] or $Ga_2[Ga_2I_6]$[7] are formally valence-isoelectronic with perchloroethane, C_2Cl_6, and exhibit Ga–Ga bonds the lengths of which are 238.7(5) and 239.2 pm, respectively. Neutral but electron-deficient monomeric compounds of the form Ga_2R_4, where R is a sterically demanding organic group, have also been characterized. Although these molecules should also feature Ga–Ga single bonds, the data show that the bond lengths are significantly greater than those determined for the dianionic species. For instance, the Ga–Ga bond length in $Ga_2[CH(SiMe_3)_2]_4$ is 254.1(1) pm.[8] It is surprising, at first glance, that the bond length in the neutral species should exceed that in a dianionic species for which coulombic repulsion is expected to be significant. The accumulated data show that a Ga–Ga single bond can adopt a variety of bond lengths with a spread of more than 15 pm. Recent studies have also produced examples of anionic species with the formula $Ga_2R_4^-$ (e.g. $[(2,4,6\text{-}i\mathrm{Pr}_3C_6H_2)_4Ga_2]^-$),[9] and the Ga–Ga bond length (234.2(2) pm) is found to be intermediate between those adopted in the neutral and the dianionic species. Finally, species of the form $Na_2Ga_2R_2$ [for example, $R = 2,6\text{-}(2,6\text{-}i\mathrm{Pr}_2C_6H_3)_2C_6H_3$] are known.[10] The unusually short Ga–Ga distance in these compounds (231.9 pm) might have been thought to indicate the presence of $[RGaGaR]^{2-}$ dianions with Ga–Ga triple bond character.[11] It has been shown subsequently, however, that the compound is better regarded as a Na_2Ga_2 cluster and that the Ga–Ga bond cannot adequately be described as a triple bond.[12,13–14] Meanwhile, the neutral compound HGaGaH was characterized in matrix-isolation experiments,[15,16] and some derivatives RGaGaR (e.g. $R = 2,4,6\text{-}i\mathrm{Pr}_3C_6H_2$)[17] were structurally analyzed. The data show that, as in the corresponding dianionic species, a *trans*-bent structure is adopted, and the long Ga–Ga distance of 262.7 pm is in agreement

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with the description of a donor–acceptor interaction between two GaR units.

In the light of all these results, a detailed characterization of an isolated Ga_2 molecule is highly desirable. This species can be generated and retained with the aid of the matrix-isolation technique. In the past we have started to study its reactivity, and interesting findings have emerged. Thus, it has been shown that Ga_2 is highly reactive, being much more willing to engage in spontaneous reactions than is a Ga atom in its ground electronic state. For example, spontaneous reaction with H_2 takes place, leading to the D_{2h}-symmetric, four-membered ring $Ga(\mu\text{-}H)_2Ga$, a species fully characterized by IR and Raman spectroscopy.[15,16] SiH_4 and SnH_4 show also signs of spontaneous reactions with Ga_2. The reaction products in these two cases are believed to be $Ga(\mu\text{-}SiH_3)GaH$ with a terminal Ga–H bond and a bridging SiH_3 unit,[18] and the *nido*-type cluster $Ga_2Sn(\mu\text{-}H)_4$, respectively (see Figure 1).[19] This superior reactivity of Ga_2 is perhaps surprising since the Ga–Ga bond in Ga_2 is quite weak (D_0 = ca. 110 kJ mol^{-1}) according to gas-phase estimates[20] and quantum-chemical calculations.[21] An analysis of the reaction mechanism for the reaction with H_2 has shown, however, that excited states of Ga_2 are involved in the reactions and that the low energy of these excited states is responsible for the reactivity.[21]

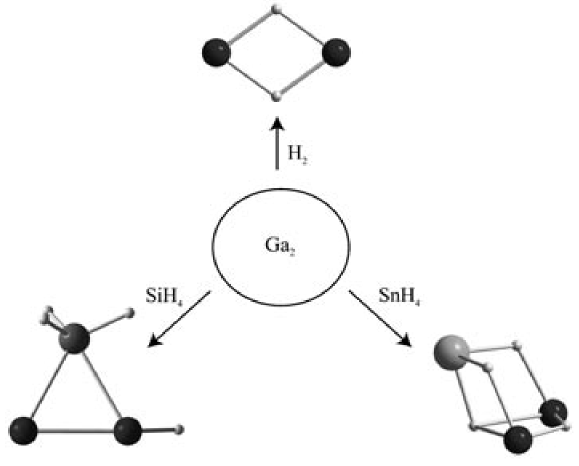

Figure 1. Spontaneous reactions of matrix-isolated Ga_2 molecules.

It is worth mentioning that quantum-chemical calculations for a diatomic like Ga_2 are not trivial and multireference methods have to be applied. There are several excited electronic states energetically close to the ground state. This has led in the past to wrong assignments. On the basis of UV/Vis experiments, for example, a $^1\Sigma_g^+$ state was first tentatively assumed to be the ground state.[22] Some DFT calculations predict a $^3\Sigma_g^-$ state to be the ground state, having a slightly lower energy (by 0.06 eV) than a $^3\Pi_u$ state.[23] However, ab initio methods favor the $^3\Pi_u$ ground state.[24–26] According to complete active-space SCF calculations followed by first-order CI[25] and multireference configuration interaction (MRD-CI) calculations,[26] the $^3\Pi_u$ state has an energy 0.05 and 0.09 eV, respectively, lower than the $^3\Sigma_g^-$ state. Very recent laser-induced fluorescence studies provide the first direct experimental evidence for a $^3\Pi_u$ ground state.[27] The energy difference between the $^3\Pi_u$ state and the $^1\Sigma_g^+$ electronic state is also small (ca. 19.0 kJ mol^{-1} for CASSCF and 46 kJ mol^{-1} for MP2 calculations).[21] According to the calculations, the three states that are still possible candidates for the ground state, $^3\Pi_u$, $^3\Sigma_g^-$, and $^1\Sigma_g^+$, differ significantly in the wavenumber of the ν(Ga–Ga) fundamental. Thus, values of 188, 238, and 153 cm^{-1}, respectively, were calculated with MP2.[21] This opens up the possibility of deciding on the ground state on the basis of Raman experiments.

Here we present the results of a thorough Raman spectroscopic investigation of isolated Ga_2 molecules at low temperatures. Some of the signals observed in our work were previously observed and already tentatively assigned to Ga_2.[28] In contrast to this previous work, though, the high resolution of our spectrometer allowed the detection of the $^{69}Ga/^{71}Ga$ isotopic pattern in the signal attributable to the vibrational fundamental and those arising from four overtones. The isotopic patterns prove not only that all the signals belong to the same molecule, but also that this molecule is indeed Ga_2. The series of overtones can be used to determine accurately the *f*(Ga–Ga) force constant in Ga_2 from the harmonic frequency. An anharmonicity constant was also determined, and the data thus allow an estimate of the dissociation energy. Finally, the bond properties of Ga_2 are compared with those of other diatomics and of known molecules containing direct Ga–Ga bonds. For elevated concentrations of gallium in the matrix, our spectra also give evidence for the presence of small gallium clusters.

Experimental Section

Gallium metal was purchased from Aldrich (99.98 %). Argon (purity 99.999 %) was used as delivered by Messer. Gallium vapor, emitted from a Knudsen-type evaporation cell at about 900 °C in a high-vacuum apparatus, was deposited together with an excess of argon on a polished copper block kept at 12 K with the aid of a closed-cycle refrigerator (Leybold LB 510). A microbalance was used to determine the rate of deposition of gallium (between 0.5 and 1.0 μg h^{-1}). Details of the matrix-isolation technique can be found elsewhere.[29]

Raman spectra were recorded with the aid of a Dilor XY800 spectrometer equipped with two pre-monochromators and a spectrograph and a CCD camera (Wright Instruments) as detector. The 514 and 488 nm lines of an Ar^+ ion laser (Coherent, Innova 90–5) were used for excitation. All spectra were recorded with a resolution of 0.5 cm^{-1}.

UV/Vis spectra were measured with an Oriel Multispec spectrograph and a photodiode array detector. An Xe-arc lamp (Oriel) was used as the light source.

Results and Discussion

Ga_2: The UV/Vis spectra of an Ar matrix containing two different concentrations of gallium are shown in Figure 2. In addition to the strong and sharp absorption at 350 nm, already assigned to the $^2S \leftarrow {}^2P$ electronic transition of Ga atoms,[27,30] the spectrum contained another, broader absorption with its maximum at 420 nm. This band has previously been tentatively assigned to Ga_2.[30,31] Another very weak and broad absorption could be found near 610 nm. The rela-

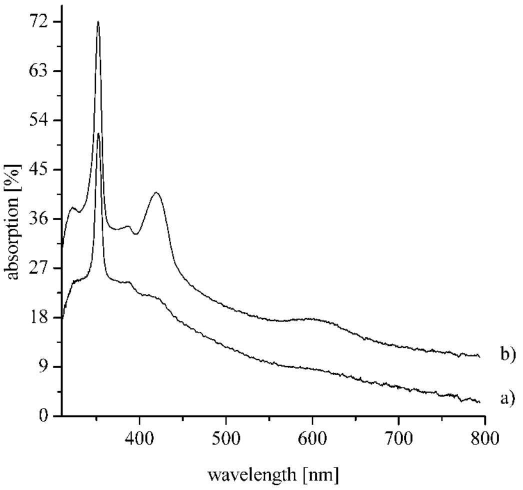

Figure 2. UV/Vis spectrum of an Ar matrix containing a low (a) and a high (b) gallium concentration.

tive intensities of the bands at 420 and 610 nm varied for different concentrations of gallium in the matrix. The two bands cannot therefore both belong to Ga_2. On the basis of experiments with different gallium concentrations, the broad feature at 610 nm (together with a very small band at about 385 nm) is tentatively assigned to Ga_3.

The 514-nm line of an Ar^+ ion laser was used in the Raman experiments. As can be seen from Figure 2, the laser line is not very close to the maximum of the band presumed to be due to Ga_2. Nevertheless, as will be shown in the following account, it was possible to detect relatively intense signals attributable to Ga_2 at low laser intensities (50 mW, 1200 s exposure time). It seems therefore that a resonance or pre-resonance effect is at work.[32] The 420 nm band has an extremely broad shoulder on the low-energy side which might be responsible for this resonance effect. Another possibility is that another electronic transition (giving rise to a weaker and undetected absorption) can be accessed at wavelengths in the order of 500 nm.

Figure 3 shows the resonance Raman spectrum obtained for Ga_2 isolated in an Ar matrix at 12 K. The spectrum is dominated by a strong signal with its maximum at 176.4 cm^{-1}. This signal contains two shoulders on its high and low energy sides (at 177.4 and 175.4 cm^{-1}). Additional, weaker signals exhibiting a clearly resolved triplet pattern were located at 348.4/350.8/353.1, 520.7/524.4/528.0, 692.0/696.6/701.1, and 861.5/867.7/874.2 cm^{-1} (Table 1). The relative intensities of the three maxima in each triplet remain unchanged for all the regions. On the other hand, the wavenumber differences between the maxima increase for triplets at higher wavenumber. Experiments with different concentrations of gallium in the matrix indicate that all these signals belong to the same species. The obvious inference is that the splitting of the signals arises from different isotopomers. The separations of one triplet and the next all lie between 170 and 177 cm^{-1}, and thus close to the wavenumber of the strongest group of signals at 175.4/176.4/177.4 cm^{-1}. On this basis we assign the signal at 175.4/176.4/177.4 cm^{-1} to the ν(Ga–Ga) fundamental and the other signals to the first four overtones of this fundamental.

Table 1. Experimentally observed wavenumbers (in cm^{-1}) for $^{69}Ga^{69}Ga$, $^{69}Ga^{71}Ga$, and $^{71}Ga^{71}Ga$.

Transition	ν($^{69}Ga^{69}Ga$)	ν($^{69}Ga^{71}Ga$)	ν($^{71}Ga^{71}Ga$)
0→1	177.4	176.4	175.4
0→2	353.1	350.8	348.4
0→3	528.0	524.4	520.7
0→4	701.1	696.6	692.0
0→5	874.2	867.7	861.5

In Figure 4 the isotopic patterns observed for the first and second overtones of Ga_2 are compared to a simulated spectrum taking into account the relative abundance of the two gallium isotopes, ^{69}Ga and ^{71}Ga (60.1:39.9). On the basis of these abundances, the presence of three bands with relative intensities of 15.9:48.0:36.1 (for $^{71}Ga^{71}Ga$:$^{69}Ga^{71}Ga$:$^{69}Ga^{69}$-Ga) is expected. The signal with the highest wavenumber in each triplet should thus belong to the $^{69}Ga^{69}Ga$ isotopomer, that with the lowest wavenumber to the $^{71}Ga^{71}Ga$ isotopom-

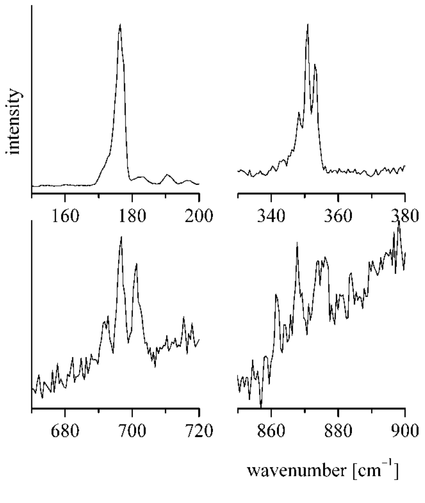

Figure 3. Resonance Raman spectrum of Ga_2 in an Ar matrix at 12 K measured with the 514-nm line of an Ar^+ ion laser.

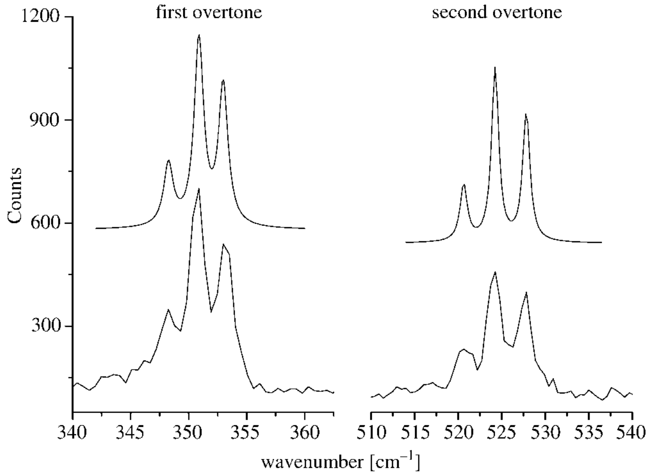

Figure 4. Bottom: Experimentally observed isotopic splitting for the first two overtones of the ν(Ga–Ga) stretch of Ga_2. Top: Simulated pattern on the basis of the natural abundances of ^{69}Ga and ^{71}Ga.

er, and that in the middle with the highest intensity to the ^{69}Ga^{71}Ga isotopomer. The simulated spectrum is in excellent agreement with the measured one.

The measured isotopic splitting leaves little doubt about the presence of more or less unperturbed Ga$_2$ molecules. On the assumption of a harmonic oscillator, the wavenumber expected for the ^{69}Ga^{71}Ga isotopomer can be calculated according to Equation (1). For example, by using Equation (1) and an observed wavenumber of 528.0 cm^{-1} in the case of $\nu(^{69}Ga^{69}Ga)$ for the second overtone, the signal due to $\nu(^{69}Ga^{71}Ga)$ is expected to occur at 524.2 cm^{-1}. The observed wavenumber of 524.4 cm^{-1} is in pleasing agreement with this estimate.

$$\nu(^{69}\mathrm{Ga}^{71}\mathrm{Ga}) = \sqrt{\frac{69+69}{71+69}}\nu(^{69}\mathrm{Ga}^{69}\mathrm{Ga}) \qquad (1)$$

Having thus established that isolated Ga$_2$ molecules are responsible for the Raman signals, we now turn our attention to the analysis of the anharmonicity and the calculation of the harmonic frequency of the molecule. The wavenumber differences between neighboring triplets decrease slightly with increasing wavenumber (175.7, 174.9, 173.1, and 173.1 cm^{-1} for ^{69}Ga^{69}Ga; 174.4, 173.6, 172.2, and 171.1 cm^{-1} for ^{69}Ga^{71}Ga; and 173.0, 172.0, 171.6, and 169.5 cm^{-1} ^{71}Ga^{71}Ga). Such results confirm that the Raman signals do indeed belong to the ν(Ga–Ga) fundamental and four overtones of a Ga$_2$ molecule, and that the potential energy curve for Ga$_2$ is not that of a harmonic oscillator. The anharmonicity constant x_e and the harmonic frequency ω_e can be determined from the difference $\Delta G(n+1 \leftarrow n)$ of the vibrational level energies $G(n+1)$ and $G(n)$ (in cm^{-1}) for the vibrational quantum numbers $n+1$ and n.[33] A plot of $\Delta G(n+1 \leftarrow n)$ as a function of $n+1$ is shown in Figure 5. According to Equation (2), the slope of the line through the experimentally obtained data points equals $-2\omega_e x_e$ and the intercept equals ω_e. Hence we obtain $\omega_e = 178.2$ cm^{-1} and $\omega_e x_e = 0.6$ cm^{-1} for ^{69}Ga^{69}Ga, $\omega_e = 177.4$ cm^{-1} and $\omega_e x_e = 0.6$ cm^{-1} for ^{69}Ga^{71}Ga, and $\omega_e = 176.3$ cm^{-1} and $\omega_e x_e = 0.7$ cm^{-1} for ^{71}Ga^{71}Ga. It is noteworthy and of immediate importance for the following discussion that the anharmonicity constant is relatively small.

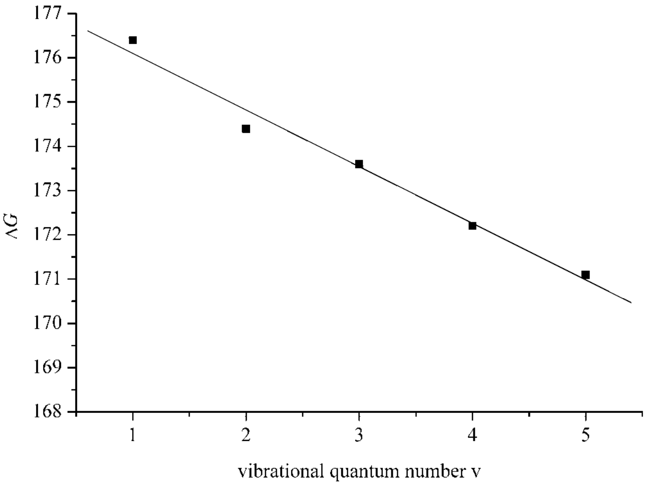

Figure 5. Determination of the harmonic frequency. The slope of the line drawn through the observed data points equals $2\omega_e x_e$ and the intersect equals ω_e.

$$\Delta G(n+1 \leftarrow n) = \omega_e - 2\omega_e x_e(n+1) \qquad (2)$$

The harmonic frequency of 178.2 cm^{-1} for the ^{69}Ga^{69}Ga isotopomer is in good agreement with the value calculated for the $^{3}\prod_{u}$ state of Ga$_2$ (188 cm^{-1})[21] and the value estimated previously (165 cm^{-1}).[34] It is, on the other hand, significantly smaller than that calculated for the $^{3}\Sigma_g{}^{-}$ state (238.4 cm^{-1}) and significantly greater than that calculated for the $^{1}\Sigma_g{}^{+}$ state (153 cm^{-1}). The experiments therefore lend cogent support to the conclusion that the $^{3}\prod_{u}$ state is indeed the electronic ground state of Ga$_2$. In this $^{3}\prod_{u}$ ground state, one of the two unpaired electrons resides in the σ_g molecular orbital formed by the two p orbitals oriented in the direction of the Ga–Ga axis. The second unpaired electron can be found in one of the two bonding π_u molecular orbitals which result from combination of the two p orbitals oriented perpendicular to the Ga–Ga axis (see also Figure 5 in ref. [21]). However, there are other configurations that contribute to a certain extent to the ground state, reflecting the fact that the angular momentum quantum number (L) is not a hard quantum number as is the sum J ($=S+L$). Nevertheless, we can conclude that a rough description of the bond properties of Ga$_2$ includes the presence of half a σ bond and half a π bond.

Having determined the harmonic wavenumbers for the three isotopomers, the force constant of Ga$_2$ can be calculated. Values of 64.5, 64.9, and 65.0 N m^{-1} were obtained for ^{69}Ga^{69}Ga, ^{69}Ga^{71}Ga, and ^{71}Ga^{71}Ga. The average of these values, 64.8 ± 0.3 N m^{-1}, is then the best estimate of the force constant on the basis of our experiments. The experimentally derived harmonic wavenumber and the anharmonicity constant can also be used to obtain a rough estimate (upper limit) of the dissociation energy of Ga$_2$. With the assumption of a Morse potential, the dissociation energy D_0 can be calculated from Equation (3). If zero-point vibrational energy corrections are included, the D_e value (upper limit) can be estimated to fall in the range 130–160 kJ mol^{-1}, comparing satisfactorily with a relatively new gas-phase estimate of about 110 kJ mol^{-1}[20] and an older estimate of 135 kJ mol^{-1}.[34]

$$D_0 = \frac{\omega_e{}^2}{4\,\omega_e x} \qquad (3)$$

It is of interest to compare the force constant and dissociation energy derived for Ga$_2$ with those of other known diatomics of the same period of the periodic table. For K$_2$ and Ca$_2$, harmonic wavenumbers of 92.0[35] and 64.9 cm^{-1},[36] respectively, have been measured. Thus, as anticipated, K$_2$ and Ca$_2$ exhibit very small force constants (f) of not more than about 10 and 5 N m^{-1}, respectively. Br$_2$ has a force constant of 246 N m^{-1}.[34] Ti$_2$ is an example of an electron-poor transition-metal dimer with a harmonic wavenumber of 407.0 cm^{-1} and $f = 234.2$ N m^{-1}.[37] On the other hand, Ni$_2$, an electron-rich transition-metal dimer, has a harmonic wavenumber of 259.2 cm^{-1} (for the ^{58}Ni^{58}Ni isotopomer), resulting in $f = 115$ N m^{-1}.[38] All these data show that the force constant of Ga_2 is relatively small.

However, knowledge of the stretching force constant is obviously not a sufficient criterion of the strength of a bond. A comparison should also take into account the dissociation energy. Since, given a Morse-type behavior, the dissociation energy is proportional not only to f but also to $(\omega_e x_e)^{-1}$, the anharmonicity is of importance in this context. As already mentioned, Ga_2 has a relatively small anharmonicity constant, so that the dissociation energy is higher than expected purely on the basis of the force constant. With a value of up to about 145 kJ mol^{-1}, it is, for example, close to that of Ti_2,[37,39] for which the force constant and anharmonicity constant are larger. It is much larger than that determined for Ca_2 (13.2 kJ mol^{-1}),[40] but smaller than that of Br_2 (193 kJ mol^{-1}).[41]

According to our CASSCF calculations, Ga_2 exhibits a bond length of 276 pm in its $^3\Pi_u$ ground state.[21] The bond length can also be estimated on the basis of the empirical but well tried relationship described by Herschbach and Laurie[42] linking stretching force constants to bond lengths (r_e). Using $f = 64.8$ N m^{-1}, a bond length r_e of 276 pm results, a value that matches exactly the one calculated by quantum chemical calculations. The bond length is significantly longer than the shortest Ga–Ga distance in α-Ga (248.2 pm).[1] The wavenumber of 246 cm^{-1} measured for the a_g ν(Ga–Ga) mode in α-Ga[3] is also not in line with the presence of isolated Ga_2 pairs in the $^3\Pi_u$ electronic ground state. For the $^3\Sigma_g^-$ excited state of Ga_2, on the other hand, a Ga–Ga bond length of 251 pm and a wavenumber of 204 cm^{-1} for the ν(Ga–Ga) mode have been calculated,[21] giving values closer to those found in α-Ga. It is interesting that the α-Ga structure is very similar in energy to the other modifications in which Ga_2 pairs are no longer present. Thus the energy differences between the Ga-II, β-, and the fcc-phase are no more than 4, 9, and 11 kJ mol^{-1}, respectively.[2] The small energy gaps may reflect the relatively small dissociation energy of Ga_2. It seems likely therefore that the characterization of isolated Ga_2 will aid an understanding of the different forms of solid Ga and also, possibly, differences in the structures of other Goup 13 elements.

Finally, the properties determined for the Ga–Ga bond in Ga_2 should be compared with those of other known molecules featuring a direct Ga–Ga bond. The Ga–Ga bond length calculated for HGaGaH is 262 pm.[15] X-ray diffraction results available for some derivatives of the type RGaGaR (e.g. R = 2,4,6-iPr$_3$C$_6$H$_2$)[17] are in excellent agreement with this value. The ν(Ga–Ga) fundamental is calculated to occur at 163 cm^{-1}. Unfortunately, this mode has not been detected in experiments. The dissociation energy of HGaGaH was calculated to be not more than 57 kJ mol^{-1}.[43] Ga_2, which has approximately half a σ bond and half a π bond, therefore exhibits a dissociation energy about twice as big as HGaGaH. This points again to the weakness of the Ga–Ga bond in HGaGaH, in line with the description of a donor–acceptor interaction.

Ga_2H_4 has been sighted in matrix-isolation experiments.[44] Derivatives such as Ga_2Cl_4 or the hydride Ga_2Cl_3H have been synthesized and characterized by single-crystal X-ray diffraction.[45,46] Like Ga_2Cl_4, Ga_2H_4 seems to prefer a C_{3v} symmetric structure, which can be described roughly as an ion pair $Ga^+[GaH_4]^-$.[47] The isomer H_2GaGaH_2 (with D_{2d} symmetry) featuring a direct Ga–Ga bond (247 pm) is about 50 kJ mol^{-1} higher in energy. The dissociation energy of the D_{2d} symmetric isomer into two GaH_2 fragments has been calculated to be about 260 kJ mol^{-1} (according to CCSD(T)).[43] If the calculations are correct, this molecule, which should exhibit a Ga–Ga σ bond, has a dissociation energy much higher than that of Ga_2. Vibrational spectra measured for $Ga_2Cl_4 \cdot 2\,L$[48] and $Ga_2I_4 \cdot 2\,L$[49] (where L are ligands, for example, THF or dioxane) span regions of 213–258 cm^{-1} and 118–145 cm^{-1}, respectively, for the ν(Ga–Ga) fundamental. UV/Vis absorptions were also assigned to transitions of electrons in the Ga–Ga bond (e.g. at ca. 370 nm for tetrakis[bis(trimethylsilyl)methyl]digallane),[50] occurring in the same range as the band detected for Ga_2 (ca. 400 nm).

Small Ga$_n$ clusters: Figure 6 compares the resonance Raman spectra recorded for two different concentrations of gallium in the matrix. The spectrum at high gallium concentrations gives evidence for a second series of signals at 212.1, 411.4, and 595.6 cm^{-1}, which might belong to Ga_3. Several theoretical studies have addressed the structure of this molecule. These studies indicate that the molecule probably adopts a cyclic structure with a $^2A_1$ ground electronic state.[23,51] Results from EPR experiments also tend to favour a $^2A_1$ ground state.[52] Unfortunately it was not possible to resolve isotopic structure within these three signals, but the anharmonicity constant is much higher than for the ν(Ga–Ga) fundamental of Ga_2. Additional signals were detected at 182.9, 190.5, 197.5, and 325.6 cm^{-1} in the experiments using high concentrations of gallium, possibly arising from larger gallium clusters.

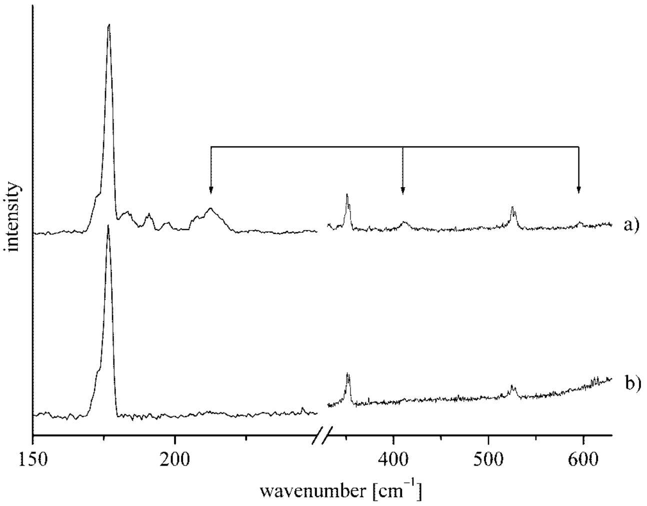

Figure 6. Comparison between the resonance Raman spectra measured for different concentrations of gallium in Ar. a:b = 1:2.

Conclusions

Ga_2 molecules isolated in an Ar matrix at 12 K have been characterized experimentally. The resonance Raman spectra give evidence for the ν(Ga–Ga) fundamental and four overtones. The two naturally occurring isotopes ^{69}Ga and ^{71}Ga cause each signal to exhibit a triplet pattern which is fully consistent with the presence of more or less unperturbed Ga_2 dimers in the matrix. The series of overtones can be used to determine the harmonic wavenumber and anharmonicity constant of Ga_2. The f(Ga–Ga) force constant is compared with those of other diatomics and molecules featuring a direct Ga–Ga bond. Using a Morse-potential model, the dissociation energy of Ga_2 in an Ar matrix can be estimated. The upper limit of about 145 kJ mol^{-1} that results invites comparison with the dissociation energies of other diatomics. The new data are of importance also to the understanding of the solid α-Ga structure, in which Ga_2 dumbbells are present. The relatively small dissociation energy of Ga_2 may also be relevant to the small energy differences between this and the other modifications of solid Ga.

With elevated concentrations of gallium in the matrix, the Raman and UV/Vis spectra also give evidence for the presence of small gallium clusters. For one of the vibrational modes, a progression possibly attributable to Ga_3 is observed. It has not been possible, however, to measure any isotopic splitting of the signals and so determine the exact number of Ga atoms in any of these clusters.

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