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Spectroscopic Evidence for a Dinitrogen Complex of Gallium and Estimation of the Ga–N_2 Bond Strength

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Abstract: Matrix-isolation experiments were performed to study the interaction between Ga atoms and N_2 by using Raman and UV/Vis spectroscopies for detection and analysis. It was revealed that a weak complex is formed, for which resonance Raman spectra were obtained. Several overtones were sighted, allowing a rough estimate of the Ga–N_2 fragmentation energy to be made (~19 kJ mol^{-1}). The excitation profile obtained from the spectra at different laser wavelengths agrees with the UV/Vis spectrum and shows that the complex exhibits an electronic transition at around 410 nm. At the Ga atom, this transition can be described as a $^2S \leftarrow ^2P$ or $^2D \leftarrow ^2P$ excitation, which is red-shifted from its position for free Ga atoms (approximately 340 nm and 270 nm for $^2S \leftarrow ^2P$ and $^2D \leftarrow ^2P$, respectively) as a result of N_2 complexation. The effect of complexation involves, therefore, only slight stabilization of the ^2P ground state but relatively strong stabilization of the excited ^2S state. Accordingly, for the Ga atom in its excited ^2S state, the Ga–N_2 bond energy can be estimated to be around 79 kJ mol^{-1}.

Keywords: matrix isolation · nitrides · quantum chemical calculations · Raman spectroscopy · semiconductors

Introduction

The detailed mechanism for formation of solid, crystalline III/V semiconductor materials, such as AlN and GaN, by means of chemical vapour deposition (CVD) or molecular beam epitaxy (MBE)[1] still remains largely unknown, despite numerous experimental and theoretical investigations in these fields. Thus, for example, in the case of MBE, it has to be differentiated between N-enriched and Ga-enriched conditions.[1c] In contrast to the bulk phases, discrete AlN and GaN molecules are highly reactive, unstable species exhibiting triplet electronic ground states [$^3\Pi$ in the case of AlN (configuration …$\pi^3\sigma^1$) and $^3\Sigma$ in the case of GaN (configuration …$\pi^2\sigma^2$)].[2,3] Thus, it is unlikely that solid AlN or GaN is formed via these molecules. In addition, the formal dimers Al_2N_2 and Ga_2N_2 have been calculated to be essentially weak complexes of the metal atoms or dimers with dinitrogen. The minimum-energy structures of molecules with the formula Al_2N_2 and Ga_2N_2 are, according to quantum chemical calculations, complexes of M_2 (M = Al, Ga) or two M atoms with N_2, resulting in either linear MMNN or MNNM molecules or a D_{2h}-symmetric M(μ-N)$_2$M molecule. The relative energies of these three possible isomers are very difficult to calculate. The D_{2h}-symmetric Ga(μ-N)$_2$Ga molecule seems to be more stable than linear GaNNGa.[4] Other calculations also argue for a D_{2h}-symmetric ground-state geometry for both Al_2N_2 and Ga_2N_2.[3] However, imaginary frequencies were obtained for the other possible isomers so that the level of theory of these calculations might not have been sufficient to characterize molecules such as GaGaNN. With other groups, we have shown already that any accurate calculations involving the metal atom dimers (Al_2 or Ga_2) themselves require the use of multireference methods.[5,6]

As the results of many experiments show that N_2 can easily leave the composite at high temperatures,[7] the interaction between the Group-13 metals and N_2 is likely to be only weak. This has stimulated several gas-phase studies on the interaction of Al,[8,9] Ga[10] or In[11] atoms and small clusters of these elements with N_2. With the help of gas-phase studies on Al·N_2, the bond energy has been estimated to be about 6 kJ mol^{-1}. For an excited state of Ga·N_2 (which is presumably the $^2\Delta$ state of the linear GaNN complex), a slightly higher bond energy of 15 kJ mol^{-1} has been estimated.[10] According to those authors, this value should be regarded as a lower limit to the true dissociation energy. Quantum chemical calculations (using the RCCSD(T) method) suggest a significantly lower interaction energy of

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4.6 kJ mol^{-1} in the case of the electronic ground state of linear Ga·N$_2$ ($^2\Pi$ state).[12] Matrix-isolation experiments have been used previously to study the reactions of laser-ablated Ga atoms with N$_2$ in solid N$_2$ matrices.[13] However, because of the energy of the laser used for ablation, some of the Ga atoms were highly excited, and N atoms were also generated by laser-induced dissociation of N$_2$. Under these conditions, linear NGaN and GaN molecules were among the products. Up to now, there exists, to the best of our knowledge, no Raman study of the interaction of Al or Ga atoms with N$_2$ under matrix conditions.

One of us has previously studied several complexes of Al and Ga atoms using the matrix-isolation technique.[14–16] For example, it has been shown that Ga forms a relatively strong complex with NH$_3$.[14] According to quantum chemical calculations, the Ga–NH$_3$ bond energy amounts to as much as about 50 kJ mol^{-1}. As a result of a Jahn–Teller effect, the complex is slightly distorted from C_{3v} symmetry.[17] The corresponding Al complex, Al·NH$_3$, has also been studied, and EPR spectroscopy has been applied in this case,[18] which gave evidence for a charge transfer from an N atom to the Al atom carrying the unpaired electron. UV/Vis data for the Ga·NH$_3$ complex showed an intense absorption around 440 nm, which was tentatively assigned to a perturbed, metal-centered $^2S \leftarrow {}^2P$ transition. Photolysis with light of this energy brings about insertion of the Ga atom into one of the N–H bonds, with the formation of the bent Ga^{II} radical, HGaNH$_2$. Additional photolysis leads to conversion of this into the Ga^{I} amide, GaNH$_2$, and the Ga^{III} amide, H$_2$GaNH$_2$ (see Figure 1).

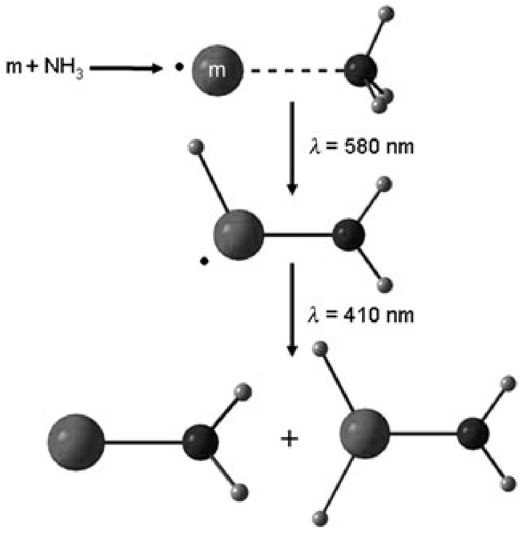

Figure 1. Pathway for the spontaneous and photolytically activated reactions taking place if Al or Ga atoms (M) are co-condensed together with NH$_3$ in an excess of solid Ar at 12 K. One of the photoproducts is the M^I amide, MNH$_2$, which possibly represents the first intermediate on the way to solid MN in CVD processes.

Results and Discussion

Below, the results obtained from Raman and UV/Vis studies are reported and discussed in turn.

Raman spectroscopy: The Raman spectrum of a solid $^{14}N_2$ matrix at 12 K is shown in Figure 2a. It consists of a very intense signal at 2327.5 cm^{-1} due to the ν(N–N) stretching fundamental.[19] At very low wavenumbers (ca. 32 cm^{-1}) another strong signal appears, which has been assigned previously to a lattice mode of N$_2$.[20]

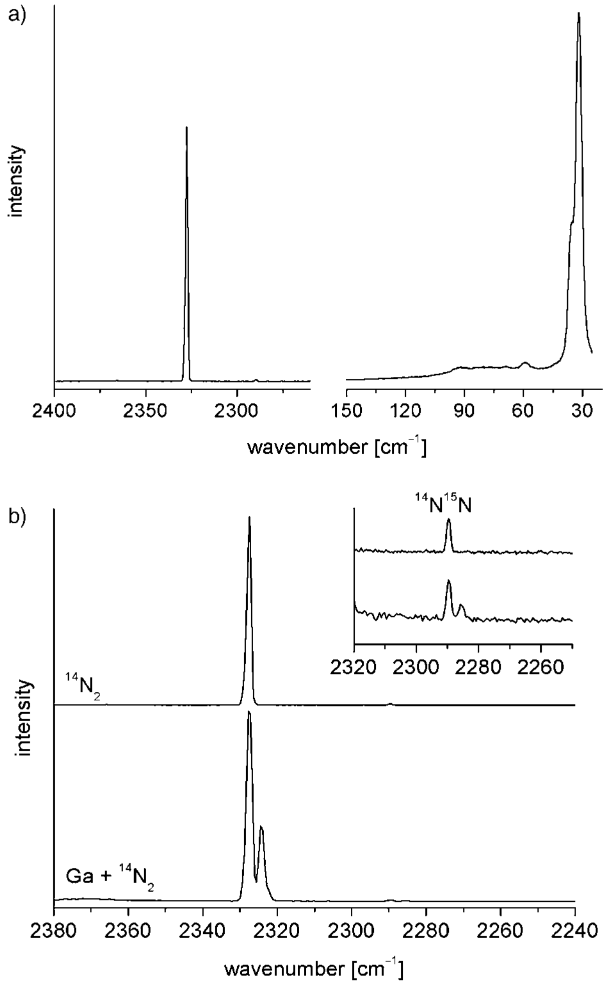

Figure 2. a) Raman spectrum measured for a solid $^{14}N_2$ matrix at 12 K. b) Comparison of the Raman spectra measured for a pure $^{14}N_2$ matrix and a $^{14}N_2$ matrix that contains gallium. Spectra were measured with an excitation radiation at 457.9 nm. The inset shows the same spectra magnified in the region around 2290 cm^{-1}.

Figure 2b compares the Raman spectrum measured for a pure $^{14}N_2$ matrix with that measured for a matrix containing Ga. In the low-wavenumber region (not shown), no changes could be monitored. In the ν(N–N) stretching region, however, a new signal (at 2324.2 cm^{-1}) was observed, which belongs in all probability to a complex between Ga atoms and N$_2$. The relatively small shift with respect to the band due to unperturbed N_2 ($-3.3\,cm^{-1}$) already indicates that the interaction is only weak. The inset shows the same spectra magnified in the region around $2290\,cm^{-1}$. The small signal traced in the spectrum of $^{14}N_2$ at $2289.6\,cm^{-1}$ belongs to the isotopomer $^{14}N^{15}N$, which is present in small quantities. The spectrum measured for a $^{14}N_2$ matrix that contains Ga atoms shows an additional signal at $2285.5\,cm^{-1}$, which can again be assigned to a complex between Ga and an N_2 species (in this case $^{14}N^{15}N$).

The experiments were repeated with different concentrations of Ga in the matrix. We deliberately chose evaporator conditions for which strong Ga_2 signals are observable in Ar matrices.[5] We also annealed the N_2 matrix after deposition to allow diffusion. However, no additional bands were observed in our Raman experiments. There was, in particular, no sign of the presence of Ga_2 molecules.[5] A possible explanation is that the complexation with N_2 prevents the Ga atoms in the matrix from dimerizing. Almost all the Ga_2 dimers observed in Ar matrices are formed in the course of, or after, deposition of the matrix and are absent from the gas phase.[6]

To obtain more information about the N_2 complex, experiments were carried out using different isotopomers of dinitrogen ($^{15}N_2$ and a 1:1 mixture of $^{14}N_2$ and $^{15}N_2$). Figure 3 illustrates the Raman spectra measured in these experiments. In the case of a $^{15}N_2$ matrix, the ν(N−N) stretching mode of unperturbed dinitrogen is red-shifted to $2249.6\,cm^{-1}$ [$\nu(^{14}N_2)/\nu(^{15}N_2) = 1.0346$]. The presence of Ga in the matrix leads again to the detection of a second signal at $2246.5\,cm^{-1}$, slightly red-shifted with respect to ν(N−N) of unperturbed dinitrogen. Measuring 1.0346, the ratio of $\nu(^{14}N_2)/\nu(^{15}N_2)$ for the complex is identical to that of free dinitrogen, indicating that this mode does not couple significantly with other modes of the complex. In the experiment involving a 1:1 mixture of $^{14}N_2$ and $^{15}N_2$, four strong signals appear. Two of these can be assigned to unperturbed dinitrogen. The other two belong to the complex and have wavenumbers that match exactly the wavenumbers measured for the complex with $^{14}N_2$ or $^{15}N_2$ alone. The half widths of the two signals due to the complex are also almost exactly the same as those measured for the experiments using $^{14}N_2$ or $^{15}N_2$ alone. Thus all indications are that the complex has the overall formula GaN_2.[21]

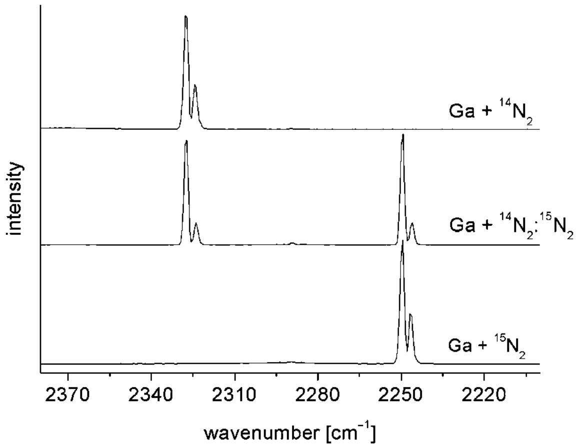

Figure 3. Raman spectra taken for Ga in solid dinitrogen matrices consisting of different dinitrogen isotopomers: a) $^{14}N_2$; b) 1:1 mixture of $^{14}N_2$ and $^{15}N_2$; c) $^{15}N_2$. Spectra were measured with an excitation radiation at 457.9 nm.

Although the data immediately shows that the complex between Ga atoms and N_2 is only very weakly bound, the Raman signal of the complex shows an interesting and distinct resonance effect. Figure 4a shows three Raman spectra measured for the same matrix but produced by excitation radiation of different wavelengths, that is, 514.5, 488.0, and 457.9 nm. The intensity of the scattering was multiplied by a factor to keep the intensity of the reference signal, ν(N−N) of unperturbed N_2 at $2327.5\,cm^{-1}$, constant. It can be seen that the intensity of the signal due to the complex between Ga atoms and N_2 depends strongly on the excitation wave-

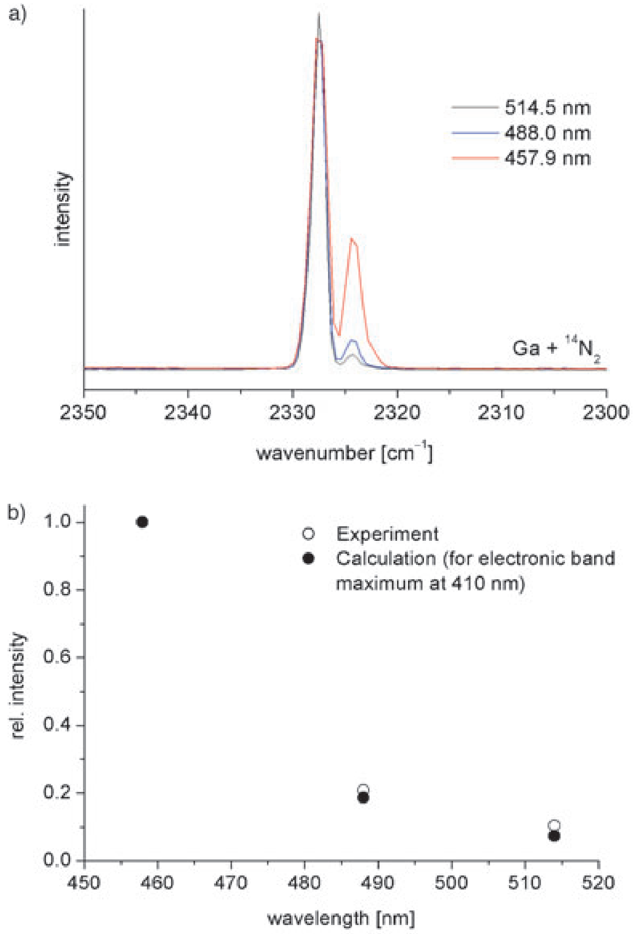

Figure 4. a) Raman spectra for Ga in a solid $^{14}N_2$ matrix produced by using different laser lines as the excitation source (514.5, 488.0, and 457.9 nm). b) Comparison between the experimental and calculated excitation profiles.

length. Thus, the signal is very intense if the 457.9 nm line of the Ar^+ ion laser is used, and relatively weak in the case of the 514.5 nm line. From this trend it follows directly that the electronic transition responsible for the resonance effect is located at wavelengths shorter than 457.9 nm. The measured intensities can be used to estimate the position of the electronic transition on the basis of an analysis of the excitation profile.[22] The intensity I_{complex} (measured relative to the reference signal) depends on the wavenumbers of the electronic band maximum, ν_r, and of the exciting radiation, ν_0, according to Equation (1).

$$I_{\text{complex}} \propto \frac{(\nu_r^2 + \nu_0^2)^2}{(\nu_r^2 - \nu_0^2)^4} \tag{1}$$

An additional factor $(\nu_{\text{complex}}/\nu_{\text{ref}})^4$ can be ignored, because it shows almost no variations. In Figure 4b, the intensities, as calculated using Equation (1) and assuming the electronic band maximum ν_r to be located at 410 nm, are compared to the experimentally observed intensities. It can be seen that the agreement is excellent. This confirms that a resonance-Raman effect is indeed operative, and that the electronic transition of the $Ga{\cdot}N_2$ complex is close to 410 nm.

It also proved possible to detect overtones of the ν(N−N) fundamental of the complex. Figures 5a and b show the regions of the Raman spectra around 4620 and 6890 cm^{-1}. A signal at 4628.9 cm^{-1} can be assigned to $2{\cdot}\nu$(N−N) of free N_2, and signals at 4620.3 and 6885.2 cm^{-1} can be assigned to $2{\cdot}\nu$(N−N) and $3{\cdot}\nu$(N−N) of the complex between the gallium atom and N_2, respectively. In addition, we have measured spectra for matrices of $^{15}N_2$ and a 1:1 mixture of $^{14}N_2$ and $^{15}N_2$ in the regions of the first overtones. The signal due to the complex between gallium and $^{15}N_2$ is located at 4466 cm^{-1}. The spectrum measured for the 1:1 mixture of $^{14}N_2$ and $^{15}N_2$ shows both the signals of $Ga^{14}N_2$ and $Ga^{15}N_2$, but no additional signals due to the same species. This is a further indication that only one N_2 molecule is coordinated to the Ga atom. There are some extra weak signals in the spectra at 4632 and 4512 cm^{-1}, but these must belong to a different species since their intensities change relative to the signals due to GaN_2 in experiments with different concentrations of gallium in the matrix.

The observed overtones can be used to estimate the difference in the N−N dissociation energy, ΔD_e, between the complex and free N_2. Applying Equation (2) (where ω_e and ω'_e denote the harmonic frequency (in cm^{-1}) of uncoordinated N_2 and coordinated N_2, respectively) gives a value of about 14.5 kJ mol^{-1} ($\omega_e x = 13.5$ cm^{-1} and $\omega'_e x' = 14.2$ cm^{-1}).

$$\Delta D_e = \frac{\omega_e^2}{4\,\omega_e \cdot x} - \frac{\omega_e'^2}{4\,\omega'_e \cdot x'} \tag{2}$$

In other words, relaxation of the N_2 unit from its equilibrium distance in the GaN_2 complex to that in uncoordinated N_2 is accompanied by an energy change of −14.5 kJ mol^{-1}. This energy will be named relaxation energy, ΔE_{relax}, in the following discussion. Equation (3) expresses the relation between the relaxation energy, the dissociation energy, and the fragmentation energy.[23]

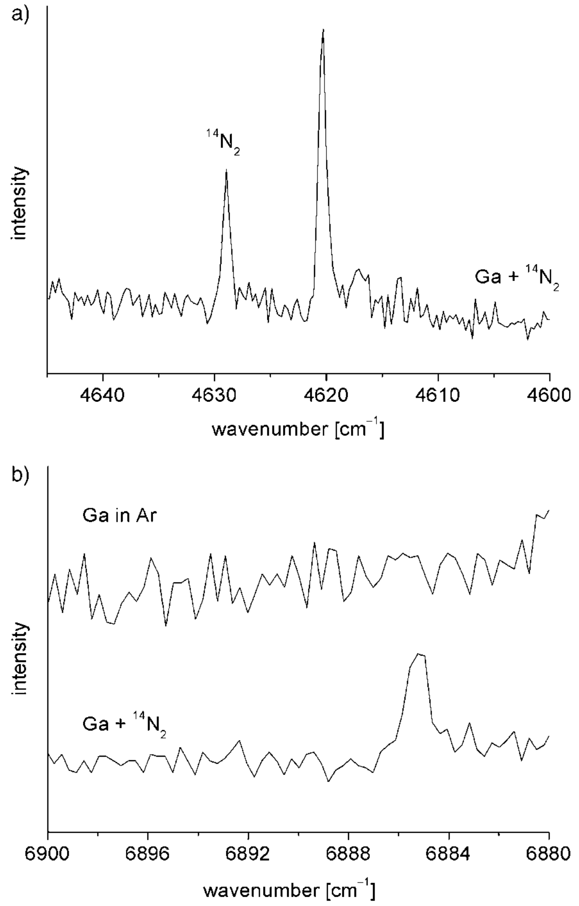

Figure 5. Regions of the Raman spectra measured for Ga in a solid $^{14}N_2$ matrix: a) around 4620 cm^{-1}, excited by the 514.5 nm laser line, and b) around 6890 cm^{-1}, excited by the 457.9 nm line of the Ar^+ ion laser.

$$\Delta E_{\text{diss}} = \Delta E_{\text{frag}} + \Delta E_{\text{relax}} \tag{3}$$

The fragmentation energy is the energy needed to cleave the Ga−N_2 bond, but keeping the N−N bond length as it is in the complex. It is thus the difference between the dissociation energy and the relaxation energy. Because the relaxation energy should always be negative, the fragmentation energy is generally larger than the dissociation energy. Previous calculations using high-level quantum chemical calculations suggested the dissociation energy to be about 4.6 kJ mol^{-1}.[12] With this value, a fragmentation energy of approximately 19.1 kJ mol^{-1} can be deduced for GaN_2.

UV/Vis spectroscopy: Figure 6a shows the UV/Vis spectrum recorded for gallium atoms isolated in an Ar matrix, together with those obtained for gallium in an N_2 matrix at different deposition times. In the first case, a strong and sharp feature appears at 340 nm, which has been assigned previously to the $^2S \leftarrow {}^2P$ transition of Ga atoms.[24] In addition, a weak, broad band shows at about 420 nm (indicated by the dotted line). This band almost certainly belongs to Ga_2.[6]

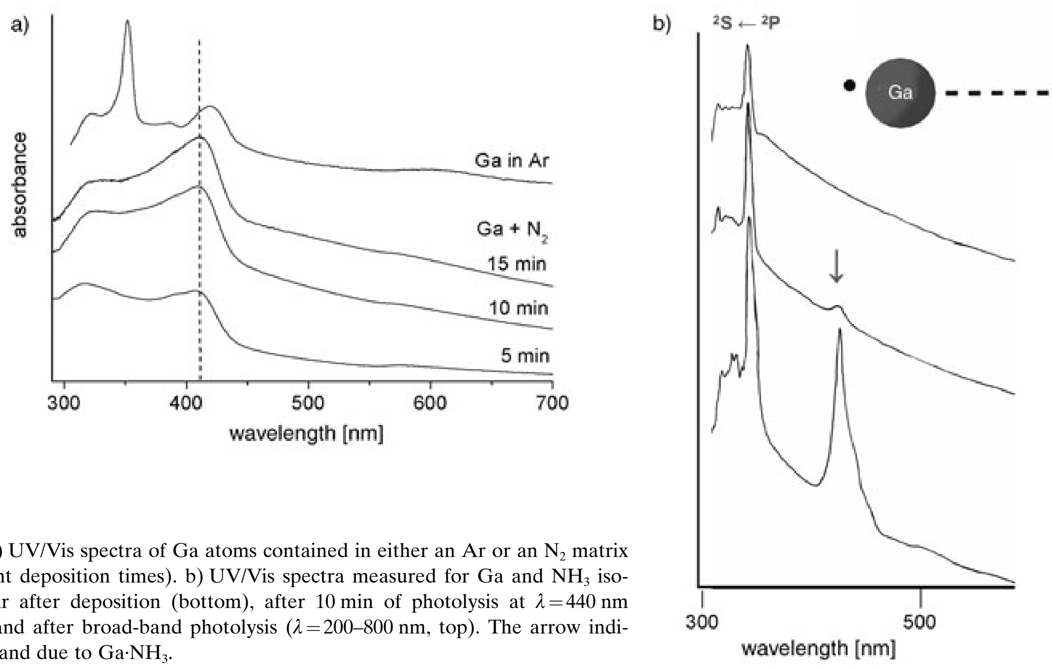

Figure 6. a) UV/Vis spectra of Ga atoms contained in either an Ar or an N_2 matrix (at different deposition times). b) UV/Vis spectra measured for Ga and NH_3 isolated in Ar after deposition (bottom), after 10 min of photolysis at $\lambda = 440$ nm (middle), and after broad-band photolysis ($\lambda = 200$–800 nm, top). The arrow indicates the band due to Ga·NH_3.

The spectra recorded with an N_2 matrix are significantly different. In these, the sharp, intense band due to Ga atoms has completely disappeared. Instead, a broad band centred at around 410 nm (ca. 290 kJ mol^{-1}) is visible. This is probably due to what is predominantly a metal-based electronic transition of the GaN_2 complex. The electronic band maximum at 410 nm is in full agreement with the analysis of the excitation profile as measured in the Raman spectra, thereby confirming that the 410 nm band belongs to the complex Ga·N_2.

For comparison, Figure 6b shows the UV/Vis spectrum recorded for the Ga·NH_3 complex formed by Ga atoms and NH_3 molecules isolated together in an Ar matrix. Because of the low concentration of NH_3 molecules in the matrix, the band due to unperturbed Ga atoms is still present. The band due to Ga·NH_3 is located at 440 nm (indicated by an arrow).

The electronic absorptions of free Ga atoms in this region occur at approximately 340 nm (ca. 350 kJ mol^{-1}) for the $^2S \leftarrow {}^2P$ transition and at about 270 nm (ca. 440 kJ mol^{-1}) for the $^2D \leftarrow {}^2P$ transition. Unfortunately, it is not possible to assign with certainty the observed absorption of the Ga·N_2 complex, but the results imply that the complexation energy is larger for one of these two excited states than for the ground state. The point is illustrated in Figure 7, on the assumption that the corresponding electronic state is indeed the ^2S state. Our resonance data has shown that the fragmentation energy of Ga·N_2 with Ga in its ^2P ground state amounts to approximately 19 kJ mol^{-1}. Very roughly, therefore, the stabilization of the former ^2P level might amount to about 19 kJ mol^{-1}. The stabilization of the excited level, $\Delta E(^2S)_{stabil}$, can then be estimated. The difference in the excitation energy between uncoordinated and coordinated Ga is around 60 kJ mol^{-1}. The excited state appears thus to be stabilized by approximately 79 kJ mol^{-1} [see Equation (4)].

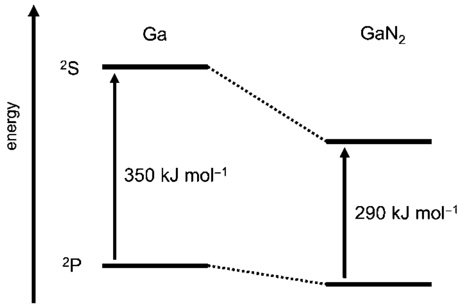

Figure 7. Effect of complexation on the electronic states of a Ga atom. The interaction between the excited electronic state of Ga and N_2 is much stronger than that between the ground electronic state of Ga and N_2.

$$\Delta E(^2P)_{stabil} + 350\,\mathrm{kJ\,mol^{-1}} = \Delta E(^2S)_{stabil} + 290\,\mathrm{kJ\,mol^{-1}} \qquad (4)$$

Although only a very rough estimate, this indicates that the interaction of N_2 with the excited state of Ga is much larger than with the ground state. Such a trend is in accord with estimates based on quantum chemical calculations for the ground-state interaction energy and the gas-phase estimates of the excited-state interaction energy.[10]

In the case of Ga·NH_3, the interaction energy for Ga in its ^2P electronic ground state should amount to about 50 kJ mol^{-1} according to quantum chemical calculations. Because of this high-energy value and the energy measured for the electronic transition (see Figure 6b), the interaction energy between Ga in its excited electronic state and NH_3 should be even larger. Thus, for both $Ga{\cdot}N_2$ and $Ga{\cdot}NH_3$, the interaction energy is higher than for the excited state of Ga. NH_3 forms a σ-dative bond with Ga in the $Ga{\cdot}NH_3$ complex. In the case of the $Al{\cdot}NH_3$ system, calculations suggest that at the first stages of the approach between Al and NH_3 the unpaired electron resides in a p orbital with A_1 symmetry (being thus oriented in the Al···N internuclear direction).[18] However, at $Al{\cdots}NH_3$ separations of about 300 pm, the unpaired orbital changes to a p orbital perpendicular to the Al···N internuclear direction. Thus, as expected, the bond is established between the filled orbital at the N atom and an empty p orbital at the Al or Ga atom. In the case of Ga in its ^2S excited electronic state, the unpaired electron is removed from the p orbital. This might lead to a stronger σ bond between NH_3 and Ga.

Conclusions

The interaction between N_2 and Ga was studied using the matrix-isolation technique, with resonance Raman and UV/Vis spectroscopic measurements being applied to the characterization of the products. The data measured for several isotopomers indicates that a 1:1 $Ga{\cdot}N_2$ complex is formed. The resonance Raman data allow an estimate of the $Ga{-}N_2$ fragmentation energy. A value of 19 $kJ\,mol^{-1}$ results for the interaction between Ga in its ground electronic state and N_2. The excitation profile was calculated on the basis of the Raman spectra excited at different wavelengths. This profile indicates that the $Ga{\cdot}N_2$ complex has an electronic transition at around 410 nm. The UV/Vis spectra do indeed give evidence for a relatively broad band at this position. The excitation energy can be related to the strength of the interaction between an excited Ga atom (presumably ^2S, but ^2D cannot be excluded) and N_2. The analysis indicates that the $Ga{-}N_2$ interaction is much stronger in the excited state of Ga than in its ground state. In the case of the $Ga{\cdot}NH_3$ complex, the data also suggests a much stronger interaction in the excited state than in the ground state. In the excited ^2S state of Ga, the electron is removed from the p orbital which possibly leads to a stronger σ bond with NH_3.

Our data is of importance for a better understanding of dinitrogen complexes of main group elements. They might also help to increase the knowledge about MBE processes designed to fabricate III/V semiconductor devices, where the formation of N_2, which might lead to nitrogen-deficient III/V materials, has to be avoided.

Experimental Section

In our matrix-isolation experiments, gallium vapour was codeposited on a copper block together with dinitrogen, in a high vacuum apparatus. The block was kept at 12 K with the aid of a closed-cycle refrigerator (Leybold, LB115). Details of the matrix-isolation technique[25] and of the apparatus used here[26] can be found elsewhere.

Raman spectra were recorded with a Jobin Yvon XY spectrometer equipped with a CCD camera (Wright Instruments, England). The spectrometer contained two pre-monochromators and a spectrograph, and the measurements were performed in the subtractive mode. The Raman spectra were produced by excitation with the 513.5, 488.0, and 457.9 nm lines of an Ar^+-ion laser (Coherent, Innova 90). All spectra were measured with a resolution of 0.5 cm^{-1}.

UV-visible spectra were recorded by using an Xe arc lamp (Oriel), an Oriel multispec spectrograph, and a photodiode array detector. A resolution of 0.5 nm was used.

Quantum chemical (DFT) calculations were carried out with the aid of the TURBOMOLE program.[27] The BP method in combination with an SVP basis set was used.

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