

Reactions of Laser-Ablated Ga, In, and Tl Atoms with Nitrogen Atoms and Molecules. Infrared Spectra and Density Functional Calculations of GaN, N_xGaN, N_xInN, and the M₃N and MN₃ Molecules

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Laser-ablated gallium atoms react with nitrogen atoms and molecules to give GaN, N_xGaN, Ga₃N, and GaN₃, which are identified from nitrogen and gallium isotopic shifts, mixed isotopic splittings, and density functional theory calculations. A 484.9 cm⁻¹ band is assigned to the GaN molecule perturbed by the nitrogen matrix, sharp 586.4 and 584.1 cm⁻¹ bands to the antisymmetric vibration of the linear N⁶⁹GaN and N⁷¹GaN molecules, 666.2 and 656.0 cm⁻¹ bands to the planar Ga₃N molecule, and 2096.9 and 1328.3 cm⁻¹ bands to antisymmetric and symmetric N–N–N vibrations of the GaNNN azide molecule. This work provides the first experimental evidence for Ga_xN_y molecules that may be involved in semiconductor film growth. Laser-ablated In and Tl atom reactions produce analogous molecules.

Introduction

Group III nitrides are important semiconducting materials due to their characteristic wide band gap.¹ Gallium nitride is particularly interesting, mainly because of its potential use for the manufacture of optoelectronic devices operating in the blue–green spectral region.² Over the past 3 decades, synthesis and characterization of semiconducting group III nitrides have been extensively researched.³ However, most of these studies were concerned with the electronic and structural properties of solid-phase materials.⁴ Electronic spectra of BN have been investigated by experiment and theory, and the ground state has been determined.^{5–8} AlN has also been observed in emission, and the vibrational fundamental has been determined.⁹ To our knowledge, no infrared spectra of the MN and M_xN_y molecules (M = Ga, In, Tl) have been reported, but a GaN film has been formed using laser ablation.¹⁰

Pulsed-laser ablation was employed for matrix infrared studies of boron atoms reacting with nitrogen in this laboratory, and several new B_xN_y species were produced and identified;¹¹ the major NBNN laser-ablated product was subsequently observed in the decomposition of boron azide.¹² Similar experiments with laser-ablated aluminum appeared to give different major products.¹³ An analogous investigation of gallium, indium, and thallium atom reactions with nitrogen was done to help identify these novel group III–V species.

Experimental Section

The technique for laser ablation and infrared matrix-isolation investigation has been described previously.¹¹ The metal targets (Ga, Aesar, 99.99999%, In, Indium Corp. of America, 99.99% Thallium, Spex, 99.999%) were mounted on a rotating rod. The 1064 nm Nd:YAG laser beam (Spectra Physics, DCR-11) was focused on the metal target surface. Laser energies ranging from 20 to 60 mJ/pulse were used in the experiments. The ablated metal atoms were co-deposited with pure nitrogen onto the 10

K CsI window at a rate of 2–4 mmol/h for 30 min to 1 h. Nitrogen (Matheson) and isotopic ¹⁵N₂ (Isotec) and ¹⁴N₂ + ¹⁵N₂, ¹⁴N₂ + ¹⁴N¹⁵N + ¹⁵N₂ (Isotec) mixtures were used. Infrared spectra were recorded with 0.5 cm⁻¹ resolution and 0.1 cm⁻¹ accuracy on a Nicolet 750 instrument. Matrix samples were annealed at different temperatures, and selected samples were subjected to broad-band photolysis by a medium-pressure mercury arc lamp (Philips, 175W) with globe removed (240–580 nm).

Results

Experimental observations for Ga, In, and Tl atom reactions with nitrogen and density functional calculations on product species will be presented.

Ga + N₂. Spectra of laser-ablated Ga atoms co-deposited with pure nitrogen are shown in Figure 1, and new product absorptions are listed in Table 1. A sharp, strong N₃ absorption¹⁴ at 1657.6 cm⁻¹, N₃⁻ at 2002.9 cm⁻¹, and weak Ga₂O band¹⁵ at 808.7 cm⁻¹ together with new product absorptions at 484.9, 584.1, 586.4, 1328.3, 1331.2, 2096.8, and 2103.6 cm⁻¹ are observed. The 2103.6, 2096.8 cm⁻¹ doublet tracks with the 1331.2, 1328.3 cm⁻¹ doublet; these bands sharpened and increased on 25 K annealing. The 2103.6/1331.2 cm⁻¹ pair disappeared on 30 K annealing and returned on 35 K annealing, while the 2096.8/1328.3 cm⁻¹ pair changed little. Another doublet at 586.4/584.1 cm⁻¹ exhibited a 3:2 intensity ratio, greatly increased on 25 K annealing, remained on 30 K annealing, and decreased on 35 K annealing. The weak 484.9 cm⁻¹ band markedly increased on 25 K annealing, but disappeared on 30 K annealing. New 666.2 and 656.0 cm⁻¹ bands produced on 25 K annealing increased together on 30 K and 35 K annealing. A similar experiment was done with higher laser power, and the 666.2 and 656.0 cm⁻¹ bands were stronger relative to other product absorptions.

Nitrogen isotopic substitution was employed for band identification; the 484.9 cm⁻¹ band shifted to 472.0 cm⁻¹, the 586.4/584.1 cm⁻¹ bands shifted to 572.1/569.9 cm⁻¹, and the 666.2, 656.0 cm⁻¹ bands shifted to 646.6, 636.6 cm⁻¹, while the doublets at 1331.2/1328.3 and 2103.6/2096.8 cm⁻¹ produced

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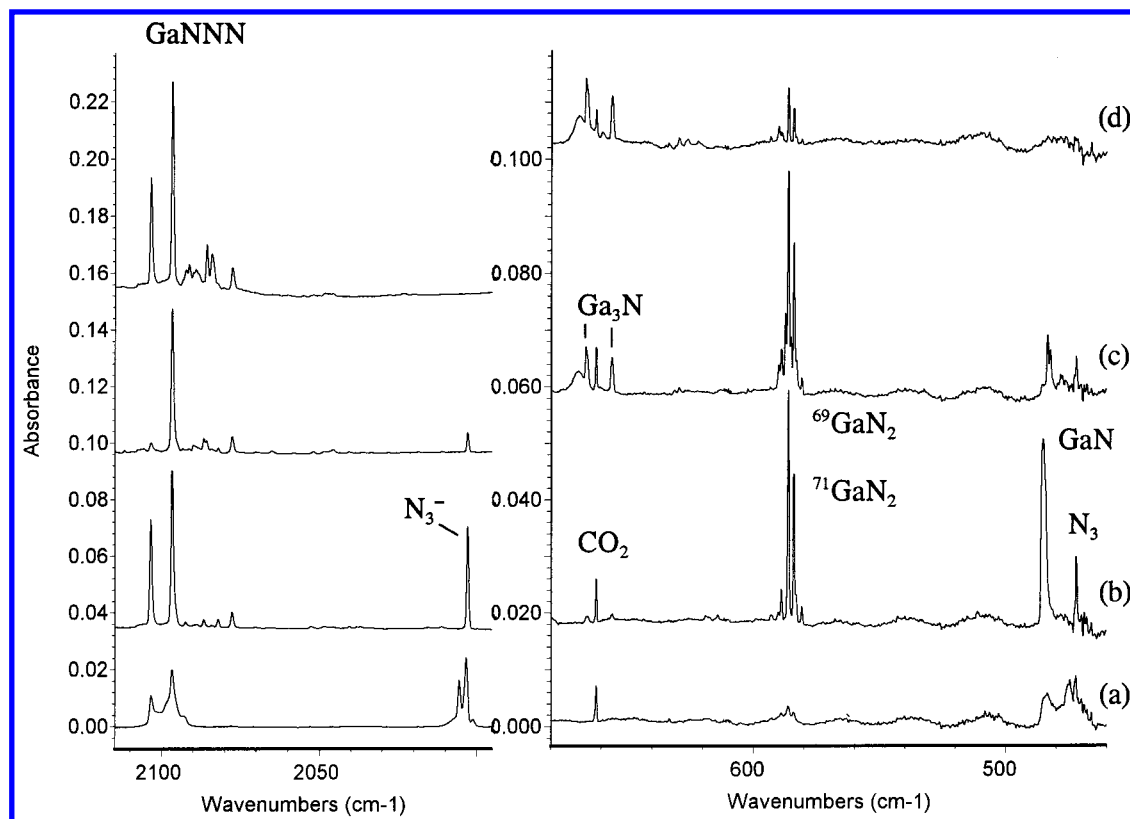


Figure 1. Infrared spectra in the 2115–1995 cm^{-1} and 680–460 cm^{-1} regions from co-deposition of laser-ablated Ga atoms with N_2 : (a) after 30 min sample deposition at 10 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K.

TABLE 1: Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Ablated Ga Atoms with Nitrogen at 10 K

$^{14}\text{N}_2$	$^{15}\text{N}_2$	$^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$	$R(14/15)$	assignment
2327.9	2250.0	2327.8, 2289.2, 2250.1	1.03462	N_2
2324.1	2246.6	2324.2, 2285.7, 2246.6	1.03450	N_2 perturbed
2103.6	2034.4	2103.6, 2099.7, 2084.3, 2079.9, 2059.3, 2054.8, 2039.4, 2034.4	1.03401	GaNNN site
2096.8	2028.0	2096.8, 2093.0, 2077.7, 2073.4, 2052.9, 2048.2, 2033.2, 2028.0	1.03393	GaNNN
2085.8	2017.2		1.03401	site
2084.3	2015.7		1.03403	site
2077.7	2009.4		1.03399	N_3^-
2005.5	1939.7	2005.5, 1995.0, 1984.0, 1961.6, 1950.9, 1939.5	1.03392	N_3^- site
2002.9	1937.5	2003.2, 1992.6, 1981.6, 1959.4, 1948.6, 1937.3	1.03375	N_3^-
1657.5	1603.3	1657.56, 1649.2, 1612.8, 1603.2	1.03391	N_3
1652.4	1598.2		1.03391	N_3 site
1331.3	1287.0		1.03443	GaNNN site
1328.3	1284.1		1.03443	GaNNN
808.7	808.6	808.7		GaOGa
757.4	735.2	754.4, 735.2	1.03020	(Ga_2N)
666.2	646.6	666.2, 646.6	1.03031	Ga_3N
656.0	636.6	656.0, 636.6	1.03047	Ga_3N
586.4	572.1	586.3, 579.1, 574.3, 572.1	1.02500	N^{69}GaN
584.1	569.9	584.1, 576.9, 572.1, 569.9	1.02492	N^{71}GaN
484.9	471.6	484.9, 471.6	1.02820	$\text{GaN}(\text{N}_2)_x$
483.4	470.0	483.3, 470.0	1.02851	$^{69}\text{GaN}(\text{N}_2)_x$
482.3	468.9	482.3, 468.9	1.02858	$^{71}\text{GaN}(\text{N}_2)_x$
472.0	456.8		1.03327	N_3

counterparts at 1287.0/1284.1 and 2034.4/2028.0 cm^{-1} . Mixed $^{14}\text{N}_2 + ^{15}\text{N}_2$ and $^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$ experiments were also done; only pure isotopic counterparts were observed for the 484.9, 666.2, 656.0 cm^{-1} bands, a quartet was observed for the

586.4/584.1 cm^{-1} bands in both mixed experiments, and a sextet was observed for the 2103.6/2096.8 cm^{-1} bands in the $^{14}\text{N}_2 + ^{15}\text{N}_2$ and an octet in the $^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$ experiment (Figures 2–4).

Argon matrix experiments were done with 4% $^{14}\text{N}_2$ and with 4% $^{15}\text{N}_2$ and gallium. The former gave 665.2 and split 586.9, 584.6 cm^{-1} bands, which increased on annealing with the 665.2 cm^{-1} feature dominating the spectrum, and the latter produced bands shifted to 645.4, 572.8, and 570.6 cm^{-1} .

In + N_2 . Similar results were obtained for the In + N_2 system. Spectra for selected regions are shown in Figure 5, and the new absorptions are listed in Table 2. Besides strong N_3 and N_3^- absorptions, a band set at 2076.6/2074.5/2073.4 cm^{-1} and an associated broad band at 1323.9 cm^{-1} were observed after deposition. These bands increased on annealing and disappeared on photolysis. A sharp band at 479.5 cm^{-1} appeared on 25 K annealing and greatly decreased on broad-band photolysis and higher temperature annealing. In addition, 25 K annealing produced two bands at 604.7, 596.3 cm^{-1} , and both markedly increased on further annealing.

Again, isotopic substitution was employed for band identification. The triplet at 2076.6/2074.5/2073.4 cm^{-1} shifted to 2008.2/2006.1/2005.5 cm^{-1} , and sextets were produced for each band in the mixed $^{14}\text{N}_2 + ^{15}\text{N}_2$ experiment. The 1323.9 cm^{-1} band shifted to 1279.6 cm^{-1} . The sharp 479.5 cm^{-1} band produced a counterpart at 466.5 cm^{-1} , and an extra 473.3 cm^{-1} band was observed in the mixed isotope experiment. The 604.7, 596.3 cm^{-1} bands gave a 586.1, 578.0 cm^{-1} partner, and no extra band was produced in the mixed isotopic experiment.

Tl + N_2 . The Tl + N_2 reaction system was simple; the single 2048.9 cm^{-1} product band observed on deposition greatly increased on 25 K annealing, decreased on photolysis, and produced a 1981.4 cm^{-1} $^{15}\text{N}_2$ counterpart. Two other bands appeared at 551.9 and 544.2 cm^{-1} on annealing, both increased

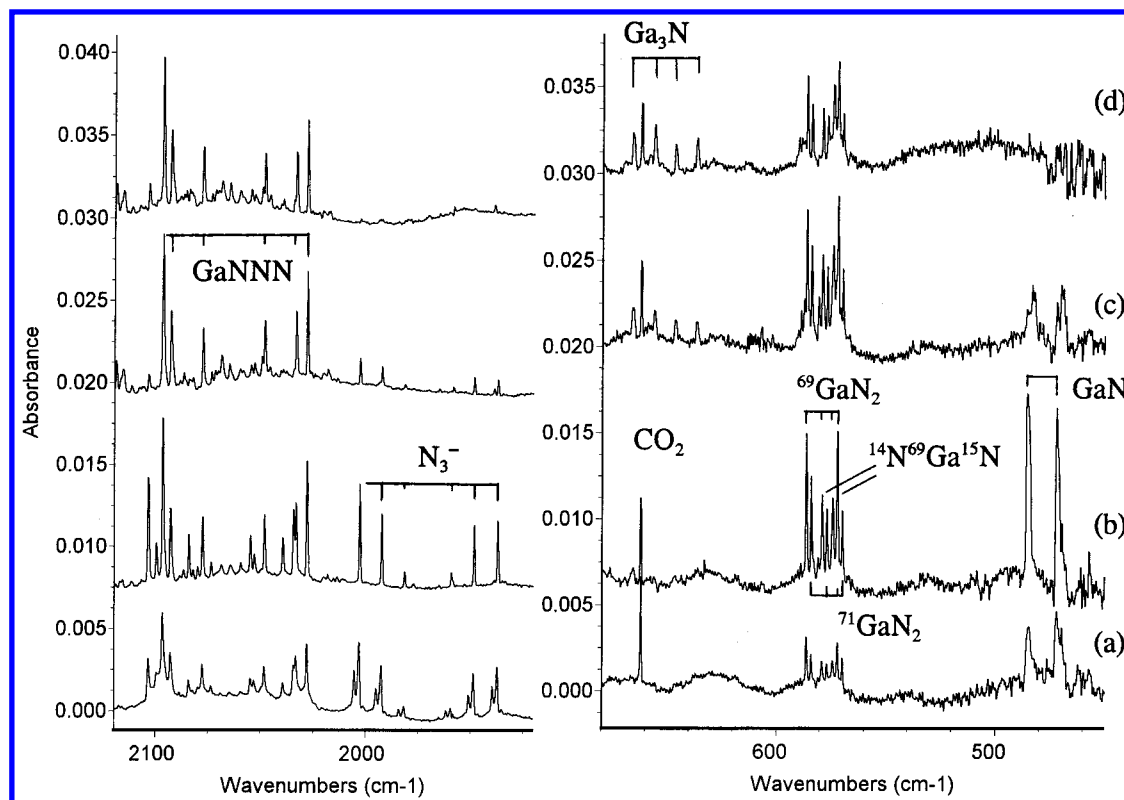


Figure 2. Infrared spectra in the 2120–1920 cm^{-1} and 680–450 cm^{-1} regions from co-deposition of laser-ablated Ga atoms with $^{14}\text{N}_2 + ^{15}\text{N}_2$: (a) after 30 min sample deposition at 10 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K.

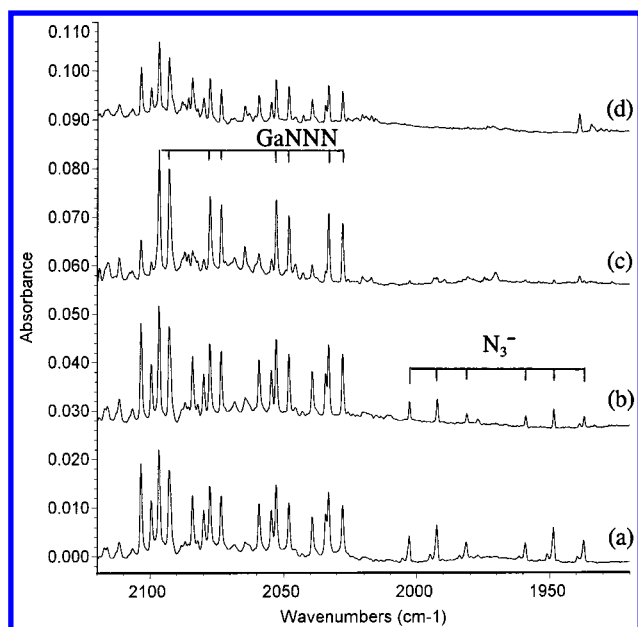


Figure 3. Infrared spectra in the 2120–1920 cm^{-1} region from co-deposition of laser-ablated Ga atoms with $^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$: (a) after 30 min sample deposition at 10 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K.

on photolysis and higher temperature annealing and gave 534.4 and 526.9 cm^{-1} $^{15}\text{N}_2$ counterparts (Table 3).

Calculations. Density functional theory (DFT) calculations were done for potential product molecules expected here using the Gaussian 94 program.¹⁶ Most calculations employed the hybrid B3LYP functional but comparisons were done with the BP86 functional as well.^{17,18} The 6-311+G* basis set was used for both Ga and N atoms,¹⁹ and the Los Alamos ECP plus DZ on In and Tl atoms.²⁰ Calculations were done for the MN, M_2N ,

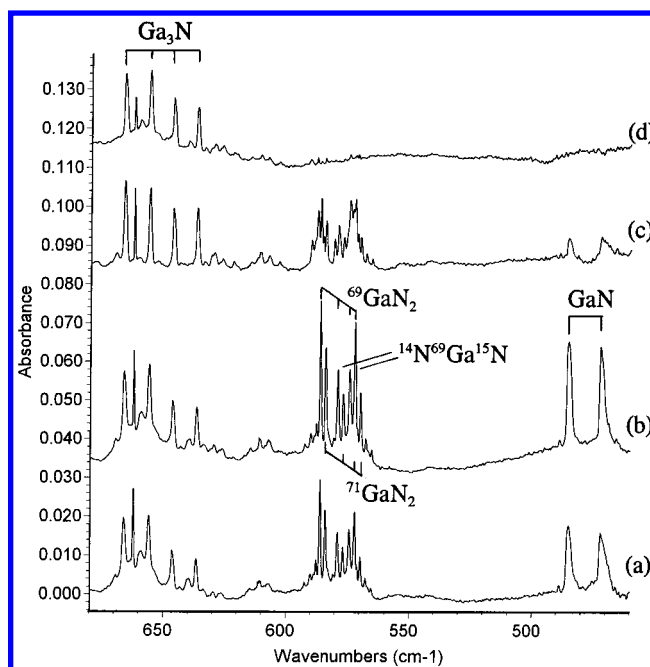


Figure 4. Infrared spectra in the 680–450 cm^{-1} region from co-deposition of laser-ablated Ga atoms with $^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$: (a) after 30 min sample deposition at 10 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K.

and M_3N molecules using both functionals, and the optimized results are listed in Table 4. The GaN molecule was determined to have a $^3\Pi$ ground state with a 1.870 Å bond length and a 580.9 cm^{-1} vibrational fundamental using B3LYP and a 1.858 Å bond length and 596.6 cm^{-1} fundamental with BP86. Two different isomers for Ga_2N namely linear GaNGa and triangle ring were calculated; the linear GaNGa doublet is more stable.

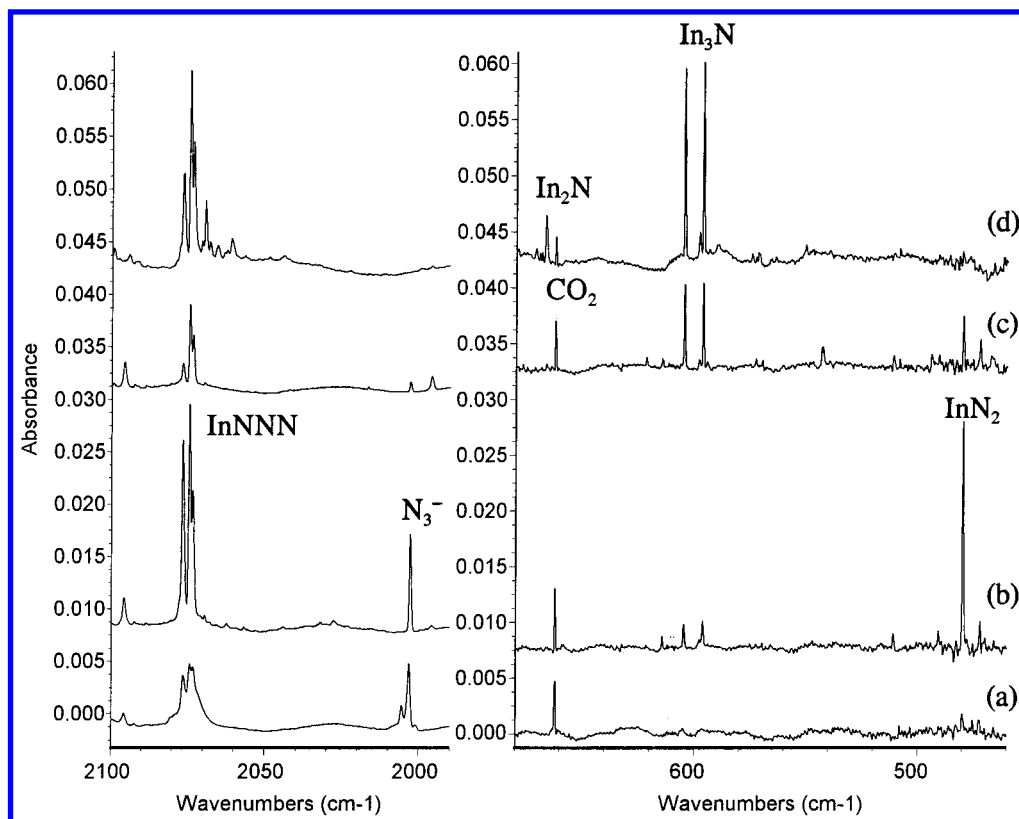


Figure 5. Infrared spectra in the 2100–1990 cm^{-1} and 680–460 cm^{-1} regions from co-deposition of laser-ablated In atoms with N_2 : (a) after 30 min sample deposition at 10 K; (b) after annealing to 25 K; (c) after annealing to 30 K; (d) after annealing to 35 K.

TABLE 2: Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Ablated In Atoms with Nitrogen at 10 K

$^{14}\text{N}_2$	$^{15}\text{N}_2$	$^{14}\text{N}_2 + ^{15}\text{N}_2$	$R(14/15)$	assignment
2327.3	2249.6	2327.9, 2250.1	1.03454	N_2
2324.5	2246.9	2324.5, 2246.8	1.03454	N_2 perturbed
2076.6	2008.2	2076.6, 2071.5, 2058.6, 2027.3, 2013.8, 2008.2	1.03406	InNNN site
2074.5	2006.1	2074.5, 2069.3, 2056.5, 2025.2, 2011.7, 2006.1	1.03410	InNNN
2073.4	2005.1		1.03406	InNNN site
2002.9	1937.1	2002.9, 1992.6, 1981.6, 1959.4, 1948.6, 1937.3	1.03397	N_3^-
1982.1	1981.5			?
1657.6	1603.3	1657.6, 1649.2, 1612.8, 1603.2	1.03387	N_3
1652.4	1598.2		1.03391	N_3 site
1437.3	1437.5			?
1323.9	1279.6		1.03462	InNNN
666.5	646.2	666.6, 646.2	1.03141	In_2N
604.7	586.1	604.7, 586.0	1.03174	In_3N
596.3	577.9	596.3, 577.9	1.03184	In_3N site
479.5	466.5	479.5, 473.3, 466.5	1.02787	NInN
472.0	456.8		1.03327	N_3

However, for Ga_3N , the B3LYP calculation for D_{3h} Ga_3N did not converge, while a slightly distorted C_{2v} structure converged and gave symmetric and antisymmetric vibrational frequencies at 640.2 and 653.4 cm^{-1} with the same isotopic ratios. The BP86 calculation for D_{3h} Ga_3N converged and gave one degenerate vibrational frequency at 631.2 cm^{-1} .

In previous transition metal atom reactions with nitrogen,^{21–23} the metal nitrides MN form dinitrogen complexes in nitrogen films. So calculations on different GaN_3 isomers were performed. Unlike transition metal systems, the NNGaN molecule is found to be unbound. Both singlet and triplet NNGaN calculations converged to $\text{GaN} + \text{N}_2$, while another isomer GaNNN was calculated to be very stable. As listed in Table 5,

TABLE 3: Infrared Absorptions (cm^{-1}) from Co-Deposition of Laser-Ablated Tl Atoms with Nitrogen at 10 K

$^{14}\text{N}_2$	$^{15}\text{N}_2$	$R(14/15)$	assignment
2327.7	2250.0	1.03453	N_2
2324.9	2247.2	1.03458	N_2 perturbed
2048.8	1981.4	1.03402	TINNN
2002.8	1937.0	1.03397	N_3^-
1657.6	1603.3	1.03387	N_3
1456.7	1431.7	1.01782	Tl^+NO^-
1357.1	1357.1		?
676.8	655.5	1.03249	?
oxide	603.6		(Tl_2N)
551.9	534.4	1.03275	Tl_3N
544.2	526.9	1.03283	Tl_3N site

the singlet GaNNN molecule is calculated to be 61.5 kcal/mol lower in energy than the triplet state and 47.3 kcal/mol lower than $\text{GaN} + \text{N}_2$.

Calculations were done for three isomers of GaN_2 . The lowest doublets of GaNN and $\text{Ga}(\text{N}_2)$ converged to $\text{Ga} + \text{N}_2$, and the results are not listed here. The NGaN molecule was calculated to have a quartet ground state, and the results are listed in Table 6. Different frequency results were obtained for the two functionals. The B3LYP calculation predicted the symmetric stretching vibration frequency lower than the antisymmetric vibration, while the BP86 calculation reversed the situation. This molecule needs higher level calculations.

Similar calculations were also done for Ga_2N_2 isomers; the calculated geometries, relative energies, vibrational frequencies, and intensities are listed in Table 7. The singlet rhombic ring (GaN)₂ and the triplet linear GaNNGa molecule, with approximately the same energy, were the most stable. The GaNGaN isomer was much higher in energy and is not listed here. Note that singlet (GaN)₂ is lower than $2\text{Ga} + \text{N}_2$ by 23.9 kcal/mol.

TABLE 4: Calculated Geometries, Vibrational Frequencies (cm⁻¹), and Intensities (km/mol) for MN, M₂N, and M₃N Molecules (M = Ga, In, Tl)

molecule	geometry	frequencies (intensities)
B3LYP		
GaN (³ Π)	Ga-N, 1.870 Å	580.9(24); ⁶⁹ Ga ¹⁵ N: 564.6(22); ⁷¹ Ga ¹⁴ N:579.5(23)
Ga ₂ N (² Σ _u ⁺)	Ga-N, 1.788 Å, linear	π _u , 64.1(32 × 2); σ _g , 297.0(0); σ _u , 867.3(4)
69/15		62.1(30), 62.1(30), 297.0(0), 840.7(4)
71/14		64.0(32), 64.0(32), 292.8(0), 866.1(4)
Ga ₃ N (¹ A ₁)	Ga ₁ N, 1.932 Å; Ga _{2,3} N, 1.918 Å,	a ₁ , 96.9(1); b ₂ , 97.1(1); b ₁ , 182.8(3); a ₁ , 255.8(0); a ₁ , 640.2(399); b ₂ , 653.4(402)
69/15		96.8(1), 96.9(1), 177.0(3), 255.8(0), 621.0(376), 633.8(379)
71/14		95.6(1), 95.7(1), 182.6(3), 252.2(0), 639.2(398), 652.4(401)
InN (³ Π)	In-N, 2.046 Å	476.2(28)
In ₂ N (² Σ _u ⁺)	In-N, 1.942 Å linear	102.0(33), 198.5(0), 759.0(6)
In ₃ N (¹ A ₁)	In-N, 2.081 Å, D _{3h}	73.4(0.5 × 2), 175.4(0), 179.6(0), 567.7(320 × 2)
TlN (³ Π)	Tl-N, 2.279 Å	365.7(49)
Tl ₂ N (² B ₂)	Tl-N, 2.163 Å; ∠TlNTl, 164.3°	104.4(7), 185.2(37), 718.4(869)
Tl ₃ N	Tl-N, 2.275 Å, D _{3h}	21.8i(16), 39.7(0), 49.4(0), 118.5(0), 495.6(392), 512.3(392)
BP86		
GaN (³ Π)	Ga-N, 1.858 Å	596.6(18); ⁶⁹ Ga ¹⁵ N: 579.9(17)(22); ⁷¹ Ga ¹⁴ N:595.2(18)
Ga ₂ N (² Σ _u ⁺)	Ga-N, 1.791 Å, linear	π _u : 54.3(27 × 2), σ _g :294.7(0), σ _u 867.8(20)
69/15		52.6(27), 52.6(27), 294.7(0), 841.2(19)
71/14		54.2(26), 54.2(26), 290.5(0), 866.7(20)
Ga ₃ N (¹ A ₁)	GaN, 1.928 Å, D _{3h}	e':91.8(1 × 2), a ₂ ':168.5(3), a ₁ ':249.1(0), e':631.2(362 × 2)
69/15		91.7(1 × 2), 163.1(3), 249.1(0), 612.3(341 × 2)
71/14		90.6(1 × 2), 168.3(3), 245.6(0), 630.2(361 × 2)
InN (³ Π)	In-N, 2.042 Å	481.5(18)
In ₂ N (² Σ _u ⁺)	In-N, 1.953 Å linear	92.4(28), 195.9(0), 750.7(16)
In ₃ N (¹ A ₁)	In-N, 2.098 Å, D _{3h}	69.2(0.4 × 2), 162.4(3), 169.2(0), 548.7(285 × 2)
TlN (³ Π)	Tl-N, 2.276 Å	359.7(39)
Tl ₂ N (² B ₁)	Tl-N, 2.167 Å; ∠TlNTl, 164.1°	107.9(5), 196.6(36), 590.0(88)
Tl ₃ N (¹ A ₁)	Tl-N, 2.292 Å, D _{3h}	100.8i(16), 36.7(0), 47.0(0), 114.1(0), 474.7(331), 498.6(330)

TABLE 5: Calculated (B3LYP) Geometries, Vibrational Frequencies (cm⁻¹), and Intensities (km/mol) for MN₃ Molecule (M = Ga, In, Tl)^a

	geometry (Å, degree)	frequency (intensity)
GaN ₃ (¹ A')	Ga-NNN, 1.933 Å; GaN-NN, 1.209 Å; GaNN-N, 1.141 Å; ∠GaNN, 149.5°; ∠NNN, 178.8°	58.0(1), 384.3(133), 595.4(15), 598.4(16), 1408.2(249), 2230.7(1080) ^b
InN ₃ (¹ Σ ⁺)	In-NNN, 2.081 Å; InN-NN, 1.203 Å; InNN-N, 1.143 Å, linear	40.4(3), 291.4(108), 621.6(19), 621.6(19), 1428.6(228), 2232.9(1100)
TlN ₃ (¹ A')	Tl-NNN, 2.323 Å; TlN-NN, 1.201 Å; TlNN-N, 1.150 Å; ∠TlNN, 162.8°; ∠NNN, 180°	56.2(6), 258.7(87), 609.7(18), 623.2(15), 1402.5(158), 2187.3(1216)

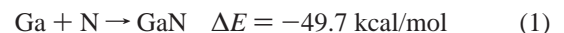
^a Both singlet and triplet MN₃ were calculated to converge to MN + N₂. ^b Frequencies for mixed isotopic molecules: 2231.4 cm⁻¹ (69-14-14-14), 2226.6 (69-15-14-14), 2178.4 (69-15-15-14), 2205.0 (69-15-14-15), 2183.1 (69-14-15-14), 2210.2 (69-14-14-15), 2161.2 (69-14-15-15), 2156.0 (69-15-15-15).

Discussion

GaN. The 484.9 cm⁻¹ band, observed after deposition, increased on 25 K annealing but disappeared on 30 K annealing. The nitrogen isotopic ratio 1.0282 is slightly lower than the diatomic harmonic GaN ratio 1.0289. In both mixed ¹⁴N₂ + ¹⁵N₂ and ¹⁴N₂ + ¹⁴N¹⁵N + ¹⁵N₂ experiments, only a doublet was observed, so only one N atom is involved in this product species, but the gallium isotopic splitting cannot be resolved. This band is observed in lower laser power experiments, so one gallium atom is probably involved. Note that the two bands produced at 483.4 and 482.3 cm⁻¹ on annealing show the appropriate gallium isotopic intensities to confirm one gallium atom. The gallium isotopic ratio 1.00228 is also quite close to the calculated GaN isotopic ratio of 1.00238.

DFT calculation predicts the ³Π ground state for ⁶⁹GaN with 580.9 cm⁻¹ vibrational fundamental, which is 96 cm⁻¹ higher than observed. Considering the scale factor of B3LYP calculations, which is 0.94 for GaNNN and 0.97 for NGaN, the observed frequency is much lower than calculated. This large matrix shift indicates that the observed GaN is not isolated and a matrix perturbation must be considered. As has been reported,²¹⁻²³ most transition metal nitrides in a nitrogen matrix prefer to form complexes (NN)_xMN, and large matrix shifts have been observed. However, DFT calculation for the NNGaN molecule converged to GaN + N₂. Note the strong GaNNN absorptions observed in our experiments, so another GaN...NN perturbation is needed. As can be seen, the calculation predicts the singlet ground state for GaNNN and the Ga-NNN stretching frequency at 384.3 cm⁻¹, which is 196.6 cm⁻¹ lower than the GaN fundamental. Because the ground state for GaN is triplet, while GaNNN is singlet, there probably exists an energy barrier between GaN + N₂ and GaNNN. Therefore, the observed 484.9 cm⁻¹ band is actually a perturbed GaN...NN complex. As will be discussed below, the GaNNN absorptions decreased on lower temperature annealing and increased again on higher temperature annealing, when the 484.9 cm⁻¹ band disappeared.

Nitrogen atoms are stable in a nitrogen matrix as shown by the ESR spectrum of bombarded solid nitrogen.²⁴ The observation of strong N₃ absorption also verifies the production of N atoms during deposition.¹¹ On annealing, reaction 1 can proceed to form GaN molecules, which is calculated to be exothermic, and nitrogen matrix perturbation can stabilize the GaN molecule. On higher temperature annealing, the GaN molecule apparently reacts with N₂ to form the more stable GaN₃ molecule.



GaN₃. The 2103.6 and 2096.8 cm⁻¹ bands were major gallium product absorptions after deposition. Both bands produced sextets in the mixed ¹⁴N₂ + ¹⁵N₂ experiment (Figure

TABLE 6: Calculated Geometry, Vibrational Frequencies (cm⁻¹), and Intensities (km/mol) for NGaN Molecule

molecule	geometry	π_u	π_u	σ_u	σ_g	
NGaN (⁴ Π_u) ^a	14-69-14	$r = 1.821 \text{ \AA}$	136.0(18)	148.4(37)	604.9(310)	621.4(0)
	14-69-15		134.4(18)	146.7(36)	593.3(240)	615.3(63)
	15-69-15		132.7(17)	144.9(35)	590.4(296)	600.4(0)
	14-71-14		135.4(18)	147.8(37)	602.4(308)	621.4(0)
NGaN (² Π_g) ^a	14-69-14	$r = 1.816 \text{ \AA}$	145.2(22)	150.9(37)	565.2(536)	632.4(0)
	14-69-15		143.5(22)	149.1(36)	557.3(512)	622.8(11)
	15-69-15		141.7(21)	147.3(36)	551.7(510)	611.0(0)
	14-71-14		144.6(22)	150.3(37)	562.9(531)	632.4(0)
NGaN (⁴ Π_u) ^b	14-69-14	$r = 1.832 \text{ \AA}$	136.3(19)	140.8(30)	641.0(79)	600.9(0)
	14-69-15		134.7(18)	139.0(30)	635.1(74)	589.1(3)
	15-69-15		133.1(18)	137.4(29)	625.6(75)	580.6(0)
	14-71-14		135.8(19)	140.2(30)	638.3(78)	600.9(0)
NGaN (² Π_g) ^b	14-69-14	$r = 1.829 \text{ \AA}$	140.6(20)	142.3(30)	647.7(72)	605.5(0)
	14-69-15		138.9(20)	140.7(30)	641.7(68)	593.6(2)
	15-69-15		137.2(20)	138.9(29)	632.2(68)	585.1(0)
	14-71-14		140.0(20)	141.8(30)	645.1(71)	605.5(0)
NInN ^c (⁴ Π_u)	$r = 1.996 \text{ \AA}$	94.1(14)	111.6(39)	472.9(272)	526.5(0)	
NInN ^c (² Π_g)	$r = 1.988 \text{ \AA}$	110.5(21)	113.9(40)	399.8(673)	538.1(0)	

^a B3LYP/6-311+G*, the ⁴ Π_u state is 14.4kcal/mol lower in energy than the ² Π_g state. ^b BP86/6-311+G*, the ⁴ Π_u state is 12.2kcal/mol lower in energy than the ² Π_g state. ^c B3LYP calculations, the ⁴ Π_u state is 15.2kcal/mol more stable in energy than the ² Π_g state.

TABLE 7: Calculated (B3LYP/6-311+G*) Geometry, Vibrational Frequencies (cm⁻¹), and Intensities (km/mol) for Ga₂N₂ Isomers

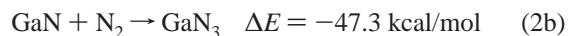
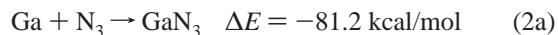
molecule	relative energy	geometry	frequencies (intensities)
(GaN) ₂ (¹ A _g) 15/69 14/71	0.0	Ga-N, 2.178 Å; N-N, 1.241 Å	b _{3u} , 134.7(3); b _{2u} , 150.7(27); a _g , 177.8(0); b _{1u} , 452.7(328); b _{3g} , 463.1(0); a _g , 1491.8(0) 130.9(3), 146.5(26), 177.8(0), 440.0(310), 447.7(0), 1441.4(0) 134.4(3), 150.3(27), 175.3(0), 451.7(327), 463.0(0), 1491.7(0)
(GaN) ₂ (³ A _u) 15/69 14/71	+56.6	Ga-N, 1.956 Å; N-N, 1.585 Å	b _{3u} , 112.4(19); b _{2u} , 235.4(37); a _g , 263.8(0); b _{1u} , 497.8(51); b _{3g} , 540.9(0); a _g , 695.0(0) 109.3(18), 228.9(35), 263.6(0), 483.9(48), 523.3(0), 672.1(0) 112.1(19), 234.9(37), 260.2(0), 496.6(51), 540.6(0), 694.7(0)
GaNNGa (² Σ_u^-) 15/69 14/71	0.0	Ga-N, 1.981 Å; N-N, 1.191 Å	π_u , 69.7(5 × 2); σ_g , 181.6(0); π_g , 208.9(0); σ_u , 455.3(388); σ_g , 1687.0(0) 67.8(5 × 2), 181.6(0), 202.0(0), 442.6(367), 1630.0(0) 69.6(5 × 2), 79.0(0), 208.9(0), 454.3(386), 1687.0(0)

2) and octets in the ¹⁴N₂ + ¹⁴N¹⁵N + ¹⁵N₂ sample (Figure 3) indicating that *three inequivalent* nitrogen atoms are involved. Two associated bands at 1331.3 and 1328.3 cm⁻¹ have the same annealing behavior, while the 14/15 isotopic ratio 1.0344 is slightly higher than the 1.0340 ratio of the upper two bands. These bands are suitable for the antisymmetric and symmetric N-N-N vibrations of the GaNNN molecule at two different matrix sites. The analogous molecules CaN₃, SrN₃, have been reported, and similar vibrations have been observed in the gas phase²⁵ as well as for solid alkali metal azides.²⁶

The assignment is in good agreement with DFT calculations. The B3LYP functional predicts the ground state of GaN₃ as singlet with linear NNN and 149.5° GaNN angle. The calculated antisymmetric and symmetric vibrational frequencies 2230.7 and 1408.2 cm⁻¹ both need a scale factor of 0.94 to fit the experimental values, which is appropriate for this B3LYP calculation.²⁷ In addition the calculated mixed nitrogen isotopic frequencies (Tables 1 and 4) are in good agreement (after scaling) with the observed values. The Ga-N stretching mode was calculated at 384.3 cm⁻¹ and could not be observed here.

The GaN₃ absorptions increased on 25 K annealing, one site disappeared on 30 K annealing, and both sites increased on 35 K annealing, suggesting that this molecule might arise from different reactions 2a and 2b. In fact, the observation of six isotopic bands in the ¹⁴N₂ + ¹⁵N₂ spectrum (Figure 2) confirms the participation of reaction 2a as only four isotopic bands can result from reaction 2b. Furthermore, the 2048.2 cm⁻¹ (Ga-15-15-14) and 2033.2 cm⁻¹ (Ga-14-15-15) band intensities are diagnostic as only the latter can arise from reaction 2b but both can be produced by reaction 2a. The fact that the 2033.2

cm⁻¹ band is 22% stronger than the 2048.2 cm⁻¹ band (the calculated infrared intensity of the 2033.2 cm⁻¹ band is only 4% greater) suggests that about 80% of the GaN₃ is formed by the N₃ radical reaction 2a. A similar conclusion can be reached from the 2093.0 cm⁻¹ (Ga-15-14-14) and 2077.7 cm⁻¹ (Ga-14-14-15) band intensities.



InN₃, TlN₃. Similar bands at 2076.6, 2074.5, and 2073.4 cm⁻¹ in the In + N₂ system can be assigned to the antisymmetric N-N-N vibration of the InN₃ molecule at different matrix sites. A broad band at 1323.9 cm⁻¹ tracks with these bands and is due to the symmetric vibration where site splitting was not resolved for this mode. In the Tl + N₂ reaction, the strong 2048.9 cm⁻¹ band is due to the analogous TlN₃ molecule.

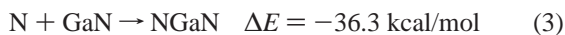
It is interesting to note that, from GaN₃ to TlN₃, the antisymmetric vibrational frequencies come close to the antisymmetric N₃⁻ vibration observed at 2002.9 cm⁻¹ in all the experiments.²⁴ The symmetric vibration for GaN₃ was about 1/8 as intense as the antisymmetric vibration, the symmetric vibration for InN₃ was only 1/18, while for TlN₃ no symmetric vibration was observed, indicating the latter is more ionic Tl⁺N₃⁻ following the alkali metal azides.²⁶

NGaN. Sharp bands at 586.4 and 584.1 cm⁻¹ appeared together on annealing, in all experiments with 3/2 relative intensity, which characterizes the vibration of one gallium atom. The 69/71 gallium ratio 1.00394 and the 14/15 nitrogen isotopic

ratio 1.0250 show more gallium and less nitrogen involvement than diatomic GaN. Both mixed $^{14}\text{N}_2 + ^{15}\text{N}_2$ and $^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$ experiments reveal quartet patterns with two weaker intermediate components, which is appropriate for the linear NGaN molecule. Interaction between stretching modes for the lower symmetry $^{14}\text{NGa}^{15}\text{N}$ molecule causes the antisymmetric mode to be weaker and the symmetric stretching mode stronger. Similar absorptions were observed in solid argon: 586.9, 584.6 cm^{-1} for $^{69,71}\text{Ga}^{14}\text{N}_2$ and 572.8, 570.6 cm^{-1} for $^{69,71}\text{Ga}^{15}\text{N}_2$, with 1.02462, 1.02453 nitrogen 14/15 isotopic ratios.

B3LYP calculations predict the ground state of NGaN molecule as $^4\Pi_u$ with a strong antisymmetric vibration at 604.9 cm^{-1} and a zero intensity symmetric vibration at 621.4 cm^{-1} just 16.5 cm^{-1} higher than the antisymmetric vibration. Similar calculations using the BP86 functional give a 641.0 cm^{-1} antisymmetric vibrational frequency, but the symmetric vibration is lower. The calculated gallium isotopic ratio 1.00415 and nitrogen ratio 1.02456 using B3LYP functional are in excellent agreement with experimental values. Furthermore, the antisymmetric stretching mode of $^{14}\text{NGa}^{15}\text{N}$ is calculated to be unusually weak, while the symmetric stretching of $^{14}\text{NGa}^{15}\text{N}$ mode is predicted to be unusually strong. This is also in agreement with the experimentally observed quartet isotopic structure (Figures 2 and 4).

The NGaN absorptions are observed on annealing, indicating that GaN arises from reaction 3, which is calculated to be exothermic by 36.3 kcal/mol. The weak complexation of N_2 to GaN cannot prevent the N atom reaction with GaN.



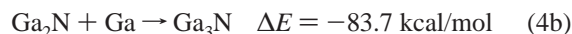
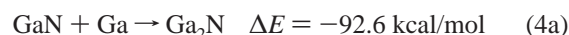
NInN. A similar band at 479.5 cm^{-1} in the In + N_2 system is assigned to the NInN molecule. This band appeared strongly on 25 K annealing and decreased on photolysis and higher temperature annealing (Figure 5). The isotopic ratio 1.02787 is lower than the diatomic InN ratio, and again, a quartet is observed in mixed isotopic experiments. This pattern is appropriate for the linear NInN molecule, which is produced by the reaction of N and InN atoms. The NInN antisymmetric vibrational frequency is 106.9 cm^{-1} lower than the NGaN frequency, and the NTIN molecule probably should be below 400 cm^{-1} and not observed in our experiment.

Ga₃N. Two bands at 666.2 and 656.0 cm^{-1} formed and increased together on annealing through all the experiments. The isotopic ratios, 1.03031 and 1.03047, are higher than the harmonic diatomic GaN ratio, 1.0289, which requires the N atom vibrating between metal atoms. In the mixed $^{14}\text{N}_2 + ^{15}\text{N}_2$ and $^{14}\text{N}_2 + ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}_2$ experiments, only pure isotopic counterparts were produced, indicating that only one N atom is involved. Unfortunately, the gallium isotopic splitting cannot be resolved here. These bands are stronger in higher laser power experiments, so Ga_xN molecules must be considered. The most stable Ga₂N molecule is calculated (B3LYP) to be the linear GaNGa doublet, which has a weak antisymmetric vibration at 867.3 cm^{-1} . However, similar calculation predicts the singlet C_{2v} Ga₃N molecule to have strong a_1 and b_2 modes at 640.2, 653.4 cm^{-1} with almost the same intensity and the same nitrogen isotopic frequency ratio 1.03092, which is in excellent agreement with observed ratios. The calculated gallium isotopic splitting is only 1.0 cm^{-1} and cannot be resolved here. Similar calculations using the BP86 functional predict the Ga₃N molecule to have D_{3h} symmetry with one strong stretching mode at 631.2 cm^{-1} . So it is difficult to determine whether these two bands are due to two different modes for the C_{2v} structure molecule or to the D_{3h} molecule at two different matrix sites. Different

sites are unlikely since the relative intensities of these two bands remain constant in all experiments, and the In₃N and Tl₃N molecules also reveal two similar bands. Therefore, these two bands are probably due to the a_1 and b_2 modes for the C_{2v} Ga₃N molecule, which undergoes a slight distortion in the nitrogen matrix. Similar distortions in solid matrixes have been observed for high-symmetry molecules.²⁸ The observation of a single 655.2 cm^{-1} band (14/15 isotopic ratio 1.03068) that dominates on annealing in solid argon suggests that the 666.2, 656.0 cm^{-1} splitting is nitrogen matrix induced and that isolated Ga₃N has D_{3h} symmetry.

Ga₂N. A weak 757.4 cm^{-1} band appears on annealing along with the 666.2 and 656.0 cm^{-1} Ga₃N bands and has almost the same 14/15 isotopic ratio, which indicates an antisymmetric Ga–N–Ga stretching mode, and again gallium isotopic splittings cannot be resolved. A mixed nitrogen isotopic doublet is formed so one N atom is involved. Our B3LYP calculation predicts the antisymmetric stretching mode of $^2\Sigma_u^+$ GaNGa at 867.3 cm^{-1} . The weak 757.4 cm^{-1} band is tentatively assigned to GaNGa. This band falls just below GaOGa at 808.7 cm^{-1} in solid nitrogen.¹⁵

The Ga₂N and Ga₃N molecules are probably formed by reactions 4, which are calculated by DFT to be highly exothermic.



In₃N, Tl₃N. Similar bands at 604.7 and 596.3 cm^{-1} in the In + N_2 system are assigned to the In₃N molecule. The relative intensities of these two bands remain constant in all experiments, the isotopic ratios, 1.03174 and 1.03184, are higher than the diatomic ratio, and only pure isotopic counterparts are observed in the mixed isotopic experiment. The 551.9 and 544.2 cm^{-1} bands in the Tl + N_2 system are likewise probably due to the Tl₃N molecule following Ga₃N and In₃N. These assignments are supported by DFT calculations (Table 4). The low imaginary frequency suggests that Tl₃N is distorted.

In₂N, Tl₂N. A weak band grows in on annealing at 666.5 cm^{-1} in concert with the strong In₃N bands at 604.7 and 596.3 cm^{-1} . This band shows the 14/15 isotopic ratio characteristic of an antisymmetric In–N–In stretching mode calculated at 759.0 cm^{-1} for the linear InNIn molecule (Table 4). This band exhibits a doublet with the $^{14}\text{N}_2 + ^{15}\text{N}_2$ sample, suggesting a single N atom vibration. The 666.5 cm^{-1} band is assigned to InNIn, which is just below InOIn at 722.0 cm^{-1} in solid nitrogen.²⁹ The thallium spectrum contains oxide³⁰ contaminants at 625.3 cm^{-1} , but a weak 603.6 cm^{-1} band in the $^{15}\text{N}_2$ experiment is appropriate for a tentative TlNTl assignment.

Conclusions

Laser-ablated gallium atoms react with nitrogen atoms and molecules to give GaN, NGaN, Ga₃N, and GaN₃, which are identified from nitrogen and gallium isotopic shifts, splittings, and density functional theory calculations. A 484.9 cm^{-1} band is assigned to the GaN molecule in the nitrogen matrix, sharp 586.4, 584.1 cm^{-1} bands for resolved gallium isotopic splitting to the antisymmetric vibration of the linear NGaN molecule, 2096.9, 1328.3 cm^{-1} bands to the antisymmetric and symmetric N–N–N vibrations of the GaNNN azide molecule, and 666.2 and 656.0 cm^{-1} bands to a distorted planar Ga₃N molecule. This work provides the first spectroscopic evidence for Ga_xN_y molecules ($x, y \geq 1$) and shows that both Ga and N atoms can add to GaN, which may help understand the mechanism of

III–V semiconductor film growth. Laser-ablated In and Tl atom reactions produced analogous molecules.

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