dipole moments, as proposed by Kuhn.<sup>18</sup>

In conclusion, among the unsymmetrical merocyanine with one alkyl chain the dye Mc[S-18,1] containing the benzothiazol ring as an electron-donating group and one methylene carbon between the rhodanine ring and the carboxyl group forms a more condensed monolayer with smaller occupied area, which is more favorable to produce the J aggregates in the mixed monolayers with methyl arachidate and *n*-hexadecane than the other dyes. According to

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the extended dipole model for the spectral properties of the resultant aggregate, the aggregation number has been estimated to be 9-10 in the two-dimensional arrangement with the transition moments closely packed parallel to each other. In addition, the mechanism of the energy transfer from the aggregate sensitizer in the monolayer systems has appeared distinct from behaviors of the monomeric sensitizer.

Registry No. Mc[O-18,1], 77404-31-0; Mc[S-18,1], 75983-37-8; Mc[Se-18,1], 77392-73-5; Mc[S-18,2], 87454-74-8; Mc[S-18,3], 104069-98-9; Mc[S-2,1], 25962-03-2; C<sub>20</sub>Me, 1120-28-1; Me(CH<sub>2</sub>)<sub>14</sub>Me, 544-76-3.

## **Reactions of Gallium Atoms<sup>†</sup>**

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Ground-state  $Ga(4p^{1} {}^{2}P_{1/2})$  atoms are produced by visible multiphoton dissociation of trimethylgallium and monitored by resonance fluorescence excitation in a pulsed laser photolysis-laser fluorescence arrangement. Reactions with  $CF_3X$  (X = F, Cl, Br, I), SF<sub>6</sub>, C<sub>2</sub>F<sub>4</sub>, N<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, 1-C<sub>4</sub>H<sub>8</sub>, and Ga(CH<sub>3</sub>)<sub>3</sub> are studied under pseudo-first-order conditions in a gas cell at room temperature. Abstraction and association reactions are observed and characterized with respect to Ar buffer gas pressure dependence. For several of the association reactions an equilibration is observed between free Ga atoms and Ga atoms bound in complexes with the reactant molecules. From measured equilibrium constants and estimated partition functions, approximate gallium atom binding energies (kcal·mol<sup>-1</sup>) are obtained for  $C_2H_4$  (9 ± 2), 1- $C_4H_8$  (9 ± 2), and  $Ga(CH_3)_3$  $(14 \pm 2)$ . Bimolecular and termolecular rate constants are reported and discussed in relation to reaction products and mechanisms.

#### Introduction

At present there is little information available on gas-phase chemical reactions of the heavier group 13 atoms Ga, In, and Tl, although the lighter members B and Al have been more extensively investigated.<sup>1</sup> Atomic Al, Ga, and In are intermediates in a number of chemical vapor deposition processes with applications in microelectronics fabrication.<sup>2</sup> Condensed-phase reactions of Al atoms and to a lesser extent Ga atoms have been investigated by low-temperature condensation techniques involving spectroscopic characterization of reaction products.<sup>3-8</sup> These techniques are however not well suited for application to chemical kinetics. There appears to be no data available on rate coefficients for gallium atom reactions.

An interesting feature of Al atom chemistry is the occurrence of both  $\pi$ - and  $\sigma$ -type complexes of Al with unsaturated organic molecules. ESR studies of cryogenic matrix deposits have shown that  $\pi$ -complexes are formed with ethylene<sup>6</sup> and benzene,<sup>7</sup> and Al-C  $\sigma$ -bonded complexes with acetylene<sup>6</sup> and buta-1,3-diene.<sup>3</sup> Similar studies have shown that both Al<sup>5</sup> and Ga<sup>4</sup> atoms react with carbon monoxide to form  $\pi$ -complexes of stoichiometry  $M(CO)_2$ . There is an indication from the ESR work that the singly occupied p-orbital of Al or Ga (with configuration  $ns^2np^1$ ) may become involved in  $\pi$ -bonding with unsaturated organic molecules in a manner analogous to that of the d-orbitals of certain transition metals, for example, in complexes with olefins.<sup>9</sup> There is however no indication from presently available results as to the stability of the Al or Ga  $\pi$ -complexes.

In this paper we present results on gas-phase reaction kinetics of ground-state  $Ga(4^2P_{1/2})$  atoms with a variety of reactants including several olefins, acetylene, benzene, and carbon monoxide. For a number of these systems equilibration is observed between free Ga atoms and Ga atoms bound in complexes with the reactant, which allows estimates of the associated binding energies. For ethylene and 1-butene we find binding energies of  $\simeq 9 \text{ kcal} \cdot \text{mol}^{-1}$ . Benzene and carbon monoxide were found to be unreactive with respect to complex formation with Ga under the conditions of our experiments, indicating considerably lower binding energies for these complexes. A number of rate constants are also reported, including termolecular rate constants for the association reactions and bimolecular rate constants for several abstraction reactions involving halogen and oxygen atom transfers.

In our experiments ground-state  $Ga(4^2P_{1/2})$  atoms are produced by visible multiphoton dissociation (MPD) of  $Ga(CH_3)_3$ . Measurements of the nascent-state distribution of gallium atoms<sup>10</sup> and of cross sections for collisional relaxation of the metastable state<sup>11</sup>

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Figure 1. Schematic diagram of laser and data acquisition system. DVM represents digital voltmeter, S/H sample and hold, AMP current amplifier, and PMT photomultiplier tube.

 $Ga(4^2P_{3/2})$  (826.2 cm<sup>-1</sup> above the ground state) have been described previously.

#### **Experimental Section**

The experimental arrangement incorporating pulsed pump and probe dye lasers is shown in schematic form in Figure 1. The pump laser produces  $Ga(4^2P_J)$  atoms by visible MPD of  $Ga(CH_3)_3$ at 461 nm, and the probe laser detects ground-state  $Ga(4^2P_{1/2})$ by resonance fluorescence excitation at 403.30 nm ( $4^2P_{1/2} \rightarrow$  $5^{2}S_{1/2}$ ). The temporal behavior of the gallium atom concentration is observed by scanning the delay time between the pump and probe laser pulses, which are produced at a repetition rate of 30 Hz. Typically the signals from 30-60 pulses are averaged at each delay setting. The computer scans the interpulse delay in preset increments and stores the kinetic data for later analysis. Details of the laser control and data acquisition systems have been described previously.12

The pump and probe XeCl excimer lasers are Lumonics Model TE-860, producing pulse widths of  $\simeq 10$  ns. The pump dye laser is a Molectron DL-100 system fitted with flowing dye cells in the oscillator and amplifier stages. The output at 461 nm is attenuated to  $\simeq 2 \text{ mJ/pulse}$  and focused into the gas cell with a 20-cm-focal-length lens. The probe dye laser is the oscillator of a Lumonics EPD-330. The output at 403.30 nm is attenuated and passed through a 1-mm-diameter aperture to produce a circular probe beam with pulse energy 10-50 nJ. The manufacturer's specified line width is 0.003 nm. The probe beam is aligned collinear and counterpropagating with the pump beam.

The gas cell is a 28 cm  $\times$  3 cm diameter Pyrex tube with angled quartz end windows and a central f/2 fluorescence collection lens which also forms the side window.  $Ga(CH_3)_3$  (Alfa electronic grade) and reactant gases were introduced into the cell from a metal high-vacuum line equipped with bellows valves. Research grade Ar, CH<sub>4</sub>, and CO and CP grade CF<sub>3</sub>Cl, (CH<sub>3</sub>)<sub>2</sub>O, and C<sub>2</sub>H<sub>2</sub> were obtained from Matheson, research grade  $N_2O$  and 1-butene from Airco and Phillips Petroleum Co., respectively, CP grade SF<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and CF<sub>4</sub> from Linde, C<sub>2</sub>F<sub>4</sub> from Columbia Organic Chemicals, and CF<sub>3</sub>Br and CF<sub>3</sub>I from SCM Specialty Chemicals. Liquid nitrogen condensable gases were vacuum distilled and/or extensively degassed before use. Infrared spectral analysis con-

Figure 2. Kinetic traces showing the  $Ga(4^2P_{1/2})$  fluorescence excitation signal as a function of time delay between pump (production) and probe (detection) laser pulses, for various gas mixtures: A, 3 mTorr of Ga-(CH<sub>3</sub>)<sub>3</sub>, 100 Torr of Ar; B, 3 mTorr of Ga(CH<sub>3</sub>)<sub>3</sub>, 0.5 Torr of CH<sub>4</sub>, 100 Torr of Ar; C, 3 mTorr of Ga(CH<sub>3</sub>)<sub>3</sub>, 5 Torr of N<sub>2</sub>O, 95 Torr of Ar. The solid curve in C is a nonlinear least-squares fit of the data points to an exponential decay.

firmed the absence of impurities. Pressure measurement was by Baratron capacitance manometers.

The fluorescence signal for detection of ground-state  $Ga(4^2P_{1/2})$ atoms corresponded to  $5^2S_{1/2} \rightarrow 4^2P_{3/2}$  emission at 417.20 nm following  $4^2P_{1/2} \rightarrow 5^2S_{1/2}$  excitation at 403.30 nm. The 417.20 nm emission was isolated from the 403.30-nm component by an interference filter (Andover 420FS10-50), which also effectively eliminated signals due to scattered light from the pump and probe laser beams. Fluorescence was detected with a cooled Hamamatsu IP28 photomultiplier tube. Linearity of the detection system with respect to gallium atom concentration was verified by monitoring the two-laser (pump and probe) signal for  $Ga(4^2P_{1/2})$  as a function of  $Ga(CH_3)_3$  pressure in the range 2-50 mTorr. The pressure of  $Ga(CH_3)_3$  used for the kinetics experiments was 3 mTorr. Fluorescence excitation was near the saturation limit, such that the fluorescence signal increased only slightly for relatively large increases in the probe laser pulse energy. This ensured that the fraction of  $Ga(4^2P_{1/2})$  atoms in the probe laser beam which became excited remained constant, independent of the gallium atom concentration.

#### Results

Shown in Figure 2 are kinetic traces representing the time dependence of the ground-state  $Ga(4^2P_{1/2})$  atom concentration for various gas mixtures made up from 3 mTorr of Ga(CH<sub>3</sub>)<sub>3</sub> and buffered to a total pressure of 100 Torr with Ar. Zero time delay corresponds to coincident pump and probe pulses, such that the newly formed gallium atoms are detected immediately (within the pump laser pulse width of 10 ns) upon fragmentation of  $Ga(CH_3)_3$ .

With only  $Ga(CH_3)_3$  and Ar in the cell, the trace shown in Figure 2A is observed. The growth of the signal at short delay times is due to relaxation of excited  $Ga(4^2P_{3/2})$  atoms to the

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TABLE I: Rate Constants for Ga(4<sup>2</sup>P<sub>1/2</sub>) Reactions<sup>a</sup>

reactant	k <sup>(2)</sup>	$\sigma/Å^2$	k <sup>(3)</sup>	$\tau/\mathrm{ps}$	Ar press./Torr	
CF <sub>1</sub> I	$(2.8 \pm 0.3) \times 10^{-10}$	80			100	
CF <sub>1</sub> Br	$(1.9 \pm 0.3) \times 10^{-10}$	52			100	
CF <sub>3</sub> Cl	$(2.2 \pm 0.3) \times 10^{-12}$	0.57			100	
$C_2 \vec{F}_4$	$(4.7 \pm 0.6) \times 10^{-13}$	0.12			100	
N <sub>2</sub> O	$(2.9 \pm 0.3) \times 10^{-13}$	0.060			100	
$S\tilde{F}_{6}$	$(8 \pm 3) \times 10^{-15}$	0.002			100	
CF₄	$(8 \pm 3) \times 10^{-15}$	0.002			100	
Ga(CH <sub>3</sub> ) <sub>3</sub>	$(1.2 \pm 0.3) \times 10^{-10}$	32			100 <sup>b</sup>	
C,H,	× ,		$(3.8 \pm 0.3) \times 10^{-30}$	60	50-500	
$1 - \tilde{C}_{A}\tilde{H}_{B}^{c}$			$(4.9 \pm 0.9) \times 10^{-30}$	90	20-200	
C <sub>2</sub> H₄			$(4.9 \pm 0.9) \times 10^{-31}$	7	50-700	
co	<10 <sup>-15</sup>		. ,		700	
C <sub>6</sub> H <sub>6</sub>	<10 <sup>-15</sup>				100	
ĊH₄	<10 <sup>-15</sup>				100	
$(CH_3)_2O^d$	<10 <sup>-15</sup>				100	
$SF_{6}$ $CF_{4}$ $Ga(CH_{3})_{3}$ $C_{2}H_{2}$ $1-C_{4}H_{8}^{c}$ $C_{2}H_{4}$ CO $C_{6}H_{6}$ $CH_{4}$ $(CH_{3})_{2}O^{d}$	$(8 \pm 3) \times 10^{-15}$ $(8 \pm 3) \times 10^{-15}$ $(1.2 \pm 0.3) \times 10^{-10}$ $<10^{-15}$ $<10^{-15}$ $<10^{-15}$ $<10^{-15}$	0.002 0.002 32	$(3.8 \pm 0.3) \times 10^{-30}$ $(4.9 \pm 0.9) \times 10^{-30}$ $(4.9 \pm 0.9) \times 10^{-31}$	60 90 7	$     \begin{array}{r}       100 \\       100^{b} \\       50-500 \\       20-200 \\       50-700 \\       700 \\       100 \\      $	

 ${}^{a}k^{(2)}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) and  $k^{(3)}$  (cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>) are bimolecular and termolecular rate constants, respectively.  $\sigma$  is a reaction cross section and  $\tau$  an effective collision complex lifetime (see text).  ${}^{b}$  In the presence of 0.5 Torr of CH<sub>4</sub>.  ${}^{c}$  But-1-ene.  ${}^{d}$  Dimethyl ether.



**Figure 3.** Plots of pseudo-first-order decay constant  $k^{(1)}$  for Ga( $4^2P_{1/2}$ ) concentration against pressure of reactant gas for C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>F<sub>4</sub>. Note that the pressure scale for C<sub>2</sub>H<sub>2</sub> is expanded by a factor (×5).

ground-state Ga( $4^2P_{1/2}$ ) induced by collisions with Ga(CH<sub>3</sub>)<sub>3</sub> and Ar.<sup>11</sup> (The nascent Ga( $4^2P_{3/2}$ )/Ga( $4^2P_{1/2}$ ) ratio is  $\simeq 2$  while the room temperature equilibrium value is 0.04.) With 0.5 Torr of CH<sub>4</sub> added to the mixture (Figure 2B), the intramultiplet relaxation is much faster, and the trace shows more clearly the relatively slow decay caused by removal of Ga( $4^2P_{1/2}$ ) by diffusion out of the probe laser detection region and reaction with Ga(CH<sub>3</sub>)<sub>3</sub>. Figure 2C shows the effect of adding 5 Torr of N<sub>2</sub>O to the Ga-(CH<sub>3</sub>)<sub>3</sub>/Ar mixture with *no* added CH<sub>4</sub>. Now the equilibration of Ga( $4^2P_J$ ) is very fast and not resolved in Figure 2C, the trace showing only a decay due to reaction of equilibrated Ga( $4^2P_J$ ) with N<sub>2</sub>O. The solid curve in Figure 2C shows a nonlinear least-squares fit of the data points to an exponential decay function.

Data for removal of  $Ga(4^2P_{1/2})$  by  $C_2H_2$ ,  $C_2H_4$ , and  $C_2F_4$  are shown in Figure 3, where the exponential decay constants are plotted against pressure of the added gas. The slopes of such plots give the bimolecular rate constants  $k^{(2)}$  for the respective reactions involving equilibrated  $Ga(4^2P_J)$  at 296 K. Results for a variety of gases including  $Ga(CH_3)_3$  are given in Table I. In most cases the kinetic traces yielded good fits to an exponential function. Distinctly nonexponential decays were however observed for several gases and representative examples are shown in Figures 4A and 5. Only for CF<sub>3</sub>Br and Ga(CH<sub>3</sub>)<sub>3</sub> were decays of the type shown in Figure 4A observed. The bimolecular rate constant for the CF<sub>3</sub>Br case was evaluated by fitting only the later parts of the decays, as illustrated in Figure 4A. For Ga(CH<sub>3</sub>)<sub>3</sub>, 0.5 Torr of CH<sub>4</sub> was added to speed up the intramultiplet relaxation, as explained above (Figure 2A,B). Ga(CH<sub>3</sub>)<sub>3</sub>/CH<sub>4</sub>, 1-C<sub>4</sub>H<sub>8</sub>, and



Figure 4. Kinetic traces as in Figure 2, showing contrasting profiles for reactions of Ga with  $CF_3Br$  and  $CF_3I$ : A, 3 mTorr of  $Ga(CH_3)_3$ , 150 mTorr of  $CF_3Br$ , 100 Torr of Ar; B, 3 mTorr of  $Ga(CH_3)_3$ , 100 mTorr of  $CF_3I$ , 100 Torr of Ar. The solid curves represent exponential decays.

 $C_2H_4$  gave decays similar to those shown in Figure 5, where the fitted curves represent functions of the type  $A \exp(-Bt) + C$ , with t the delay time and A, B, and C constant parameters for a given pressure of reactant gas. In these cases the rate constants were obtained by plotting the exponential decay constants B against pressure, as in the plot for  $C_2H_4$  in Figure 3. Justifications for these procedures are given later.

For the reactions involving  $C_2H_2$ ,  $C_2H_4$ , and  $1-C_4H_8$ , a linear dependence of the exponential decay constant on the Ar pressure was observed over the pressure ranges indicated in Table I. No Ar pressure dependence was observed for the other reactions. The results for  $C_2H_2$ ,  $C_2H_4$ , and  $1-C_4H_8$  obtained at 100 Torr of Ar are therefore expressed as termolecular rate constants  $k^{(3)}$ .  $\tau$  in Table I gives the effective collision complex lifetime, obtained by dividing the termolecular rate constant by the product of the Ga/reactant and Ar/complex collision frequencies. The latter were calculated assuming collision diameters of 4 Å for all species.  $\sigma$  gives the reaction cross sections associated with the bimolecular rate constants.

The uncertainties in Table I represent three standard deviations  $(\pm 3\sigma)$  for single data sets such as those plotted in Figure 3. Repeated measurements for several cases fell within these limits, which we take as estimates of the overall experimental uncer-



Figure 5. Kinetic traces as in Figure 2, showing decays of the form A exp(-Bt) + C for removal of Ga by but-1-ene: A, 3 mTorr of Ga(CH<sub>3</sub>)<sub>3</sub>, 3 Torr of  $1-C_4H_8$ , 97 Torr of Ar; B, 3 mTorr of Ga(CH<sub>3</sub>)<sub>3</sub>, 9 Torr of  $1-C_4H_8$ , 91 Torr of Ar; C, 3 mTorr of Ga(CH<sub>3</sub>)<sub>3</sub>, 12 Torr of  $1-C_4H_8$ , 88 Torr of Ar.

tainties. The results for SF<sub>6</sub> and CF<sub>4</sub> are subject to greater uncertainty because of the slowness of the reactions and the possibility that trace impurities accounted for some of the Ga- $(4^2P_{1/2})$  decay. At higher pressures of the reactant gases ( $\geq 100$ Torr) the fluorescence signal was effectively quenched, which put an upper limit on the working pressure range. The rate constants given for the apparently unreactive systems CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, CO, and (CH<sub>3</sub>)<sub>2</sub>O therefore represent upper limits.

#### Discussion

1. Reaction Products. Two types of reactions of gallium atoms may be distinguished on the basis of the Ar pressure dependence of the reaction rate. These are abstraction and association reactions, as exemplified by  $Ga + CF_3I \rightarrow GaI + CF_3$  and  $Ga + C_2H_4 \rightarrow Ga[C_2H_4]$ , respectively, where  $Ga[C_2H_4]$  represents a complex in which Ga is bonded to  $C_2H_4$ . A buffer gas pressure dependence arises for the association reactions because of the requirement for stabilization of the collision complex, but no such requirement holds for the abstraction reactions. A classification of the observed reactions is made in Table II, which also gives estimates of reaction exothermicities for the assumed products.

Although no direct information is available on the identity of the reaction products, those specified in Table II are reasonable in terms of the thermochemistry and the expected pattern of reactivity for a metal atom. Except for the reaction involving  $Ga(CH_3)_3$ , the association reactions could be unambiguously identified as such by the Ar pressure dependence of the reaction rate. The rate constant for the  $Ga(CH_3)_3$  reaction (Table I) is near the gas kinetic limit, so the associated activation energy must be small. A process involving abstraction of H or CH<sub>3</sub> from  $Ga(CH_3)_3$  would be expected to show a relatively large activation energy, so an abstraction mechanism seems unlikely for this case. Furthermore, the evidence presented below that the reaction is reversible under our experimental conditions strongly supports the assumption of an association reaction. The nature of the Ga

TABLE II: Reactions of Ga(4<sup>2</sup>P<sub>1/2</sub>)

C<sub>2</sub>H<sub>₄</sub>

	-,	
	Abstraction Reaction	ns
reactant	products	$-\Delta H^{\circ}_{298}^{a}/(\text{kcal}\cdot\text{mol}^{-1})$
CF <sub>1</sub> I	GaI + CF <sub>3</sub>	28
CF <sub>3</sub> Br	$GaBr + CF_3$	35
CF <sub>3</sub> Cl	$GaCl + CF_{3}$	29
C₂F₄	$GaF + C_2F_3$	<b>≃</b> 40
$N_2O$	$GaO + N_2$	$\simeq 30$
$SF_6$	GaF + SF,	<b>≃</b> 70
CF₄	$GaF + CF_3$	8
	Association Reaction	ns
reactant	products	$\Delta E^{\circ b}/(\text{kcal·mol}^{-1})$
Ga(CH <sub>3</sub> ) <sub>1</sub>	Ga[Ga(CH <sub>3</sub> ) <sub>3</sub> ]	14 ± 2
$C_2H_2$	$Ga[C_2H_2]$	
1-C,H.	Ga[1-CAHe]	9 ± 2

<sup>a</sup>Estimated standard enthalpy change for the reaction  $Ga(4^{2}P_{1/2})$  + reactant  $\rightarrow$  products at 298 K (thermochemical data from ref 14 and 15). <sup>b</sup>Estimated dissociation energy of the complex to produce Ga- $(4^{2}P_{1/2})$  + reactant at 0 K (see the text).

9 ± 2

Ga[C<sub>2</sub>H<sub>4</sub>]



Figure 6. Plots of the ratio C/A, defined by the assumed time dependence of the Ga concentration,  $A \exp(-Bt) + C$ , against the reciprocal of the pressure of the added gas for  $1-C_4H_8$ ,  $Ga(CH_3)_3$ , and  $C_2H_4$ . The slopes give the equilibrium constants for complex formation with Ga. Note that the abscissa for  $Ga(CH_3)_3$  is contracted by a factor  $(+10^3)$ .

association complexes suggested in Table II is discussed in subsection 4. In subsection 3 below estimates are made of the Ga atom binding energies for these complexes.

For the reactions of Ga with  $Ga(CH_3)_3$ ,  $C_2H_4$  and  $1-C_4H_8$ , nonexponential decay traces of the type shown in Figure 5 were observed. In all cases it was confirmed through studies of the probe laser excitation spectrum that throughout the full delay time interval the signal was associated with  $Ga(4^2P_{1/2})$  atoms. In addition, the form of the decay trace was in all cases insensitive to variations in the pulse energy of the probe laser, including pulse energies lower than that required for saturation of the Ga resonance transition. This rules out the possibility that the nearly constant background signal appearing at long times arose from Ga atom detection by way of probe laser photodissociation of a gallium-containing molecular species, for example, a reaction product. The magnitude of the background signal relative to the initial signal showed no dependence on the Ar pressure, but was inversely related to the pressure of the reactant. This is illustrated in Figure 6, which shows plots of the ratio C/A against the inverse of the pressure of added reactant. C and A are defined by the assumed functional form of the signal  $A \exp(-Bt) + C$ , which was used in the nonlinear least-squares fitting procedure (see Figure

The above observations are suggestive for an equilibration process for the association reactions

$$Ga + Q \stackrel{k_1}{\underset{k_{-1}}{\longleftarrow}} GaQ$$
 (1)

where  $k_1$  and  $k_{-1}$  represent effective bimolecular and unimolecular rate constants, respectively. The equilibrium 1 implies the following time dependence for the Ga concentration

$$\frac{[Ga]}{[Ga]_0} = \frac{k_{-1}}{(k_{-1} + k_1[Q])} + \frac{k_1[Q]}{(k_{-1} + k_1[Q])} \exp\{-(k_{-1} + k_1[Q])t\}$$
(2)

where  $[Ga]_0$  is the initial value. It is assumed that the total concentration of gallium as Ga and GaQ is conserved (i.e., there are no other loss mechanisms for Ga), and that initially all of the gallium is present as free atoms. The right-hand side of eq 2 has the form  $A \exp(-Bt) + C$ , which is the same form used for curve fitting the decay traces. It is seen from eq 2 that  $C/A = k_{-1}/k_1[Q]$ . The inverse dependence of the ratio C/A on the pressure of the reactant illustrated in Figure 6 for Ga(CH<sub>3</sub>)<sub>3</sub>, 1-C<sub>4</sub>H<sub>8</sub>, and C<sub>2</sub>H<sub>4</sub> is thus consistent with the assumption of an equilibration process. The equilibrium constant (in pressure units) associated with (1) is

$$K_{\rm p} = \frac{p({\rm Ga})p({\rm Q})}{p({\rm Ga}{\rm Q})} = \frac{k_{-1}}{k_{\rm 1}}RT \tag{3}$$

and thus the slopes of the plots of C/A against 1/p(Q) in Figure 6 give the values of  $K_p$ . Note that p(Q) = [Q]RT, where R is the gas constant and T the absolute temperature.

The equilibrium 1 may be written in terms of elementary processes as follows

$$Ga + Q \xrightarrow{k_2} GaQ^*$$
 (4a)

$$GaQ^* + Ar \xrightarrow{k_3} GaQ + Ar$$
 (4b)

where GaQ<sup>\*</sup> represents the unstabilized collision complex,  $k_2$ ,  $k_3$ , and  $k_{-3}$  are bimolecular rate constants, and  $k_{-2}$  is a unimolecular rate constant. With a stationary-state assumption for [GaQ]\*,  $k_1$  in eq 2 may be written as

$$k_1 = \frac{k_2 k_3 [\text{Ar}]}{k_{-2} + k_3 [\text{Ar}]}$$
(5)

The termolecular rate constants in Table II should be interpreted as in eq 5. The observation of a linear dependence of the apparent bimolecular rate constant on the Ar pressure implies  $k_{-2} \gg k_3$  [Ar]. In the case of the reaction with  $Ga(CH_3)_3$ , with a pressure-independent rate in the range 20-300 Torr of Ar, the implication is that  $k_3[Ar] \gg k_{-2}$ .

2. Kinetics. The ground  $Ga(4^2P_{1/2})$  and excited  $Ga(4^2P_{3/2})$ states of gallium (hereafter designated Ga and Ga', respectively) are interconverted by fine-structure changing (fsc) collisions, which in the absence of reactive processes act to establish the room temperature equilibrium ratio  $\gamma = [Ga]_{eq}/[Ga']_{eq} = 27.7$ . If for a particular added gas Q reactive collisions have low probabilities relative to fsc collisions, then equilibrium is attained, and the decay rates of the equilibrated Ga and Ga' concentrations due to reactions with Q are equal and given by the pseudo-first-order decay constant

$$\{\gamma k/(1+\gamma) + k'/(1+\gamma)\}[Q] \simeq \{0.97k + 0.03k\}[Q]$$

Here k and k' are bimolecular rate constants for reactions of Ga and Ga', respectively. It is anticipated on the basis of earlier work<sup>11</sup> that the rate constants for fsc collisions of  $Ga(4^2P_{3/2})$  with polyatomic molecules are generally large. Thus the relatively small rate constants given for CF<sub>3</sub>Cl, C<sub>2</sub>F<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>, and CF<sub>4</sub> in Table I should be interpreted as containing both k and k' in the above linear combination.

The rate constants for CF<sub>3</sub>I and CF<sub>3</sub>Br in Table I are near the gas kinetic limit. In this situation the observed decay constant for the Ga concentration is attributable to the reaction of Ga alone, since the Ga  $\rightarrow$  Ga' fsc rate (with maximum value  $\simeq$ (gas kinetic rate)/ $\gamma$ ) may be neglected in relation to the Ga reaction rate. Thus for CF<sub>3</sub>I and CF<sub>3</sub>Br the rate constants apply specifically for ground-state  $Ga(4^2P_{1/2})$  reactions. The time dependence of the Ga concentration for this case is given by

$$\frac{[Ga]}{[Ga]_0} = \left[\frac{-\alpha k_Q'}{k' - k + k_Q'}\right] \exp\{-(k_Q' + k')[Q]t\} + \left[1 + \frac{\alpha k_Q'}{k' - k + k_Q'}\right] \exp\{-k[Q]t\}$$
(6)

where k(k') and  $k_Q(k_Q')$  are bimolecular rate constants for reaction and fsc collisions of Ga (Ga'), respectively, and  $\alpha$  is the ratio of the initial concentrations.

$$\alpha = [Ga']_0 / [Ga]_0 \simeq 2$$

The value of  $\alpha$  is taken from the results of an earlier study<sup>10</sup> of the visible multiphoton dissociation of  $Ga(CH_3)_3$ .

The first term in eq 6 represents a growth term in [Ga] due to equilibration of the [Ga]/[Ga'] concentrations from the initial ratio  $1/\alpha \simeq 0.5$  to the equilibrium value  $\gamma = 28$ . The second term accounts for the decay of [Ga] due to reaction, with rate constant k, as noted above. The appearance of the kinetic trace for the Ga concentration depends on the relative magnitudes of the quantities  $k_Q'$  and |k'-k|. It may be seen from eq 6 that in the case where  $k_Q' \ge |k'-k|$ , the [Ga] profile has a significant growth component due to Ga'  $\rightarrow$  Ga fsc collisions, and when  $k_Q'$  $\ll |k'-k|$ , no such growth component appears and the decay is exponential in form. Examples of this effect are shown in Figure 4. The trace for CF<sub>3</sub>Br in Figure 4A has a flat-topped appearance due to the growth component, while that for CF<sub>3</sub>I in Figure 4B shows only an exponential decay. It may be concluded from this that the Ga' fsc/reaction branching ratio  $k_0'/k'$  is larger for CF<sub>3</sub>Br than for CF<sub>3</sub>I. This is understandable in terms of a larger value of k' in the case of the  $Ga' + CF_3I$  reaction, possibly reflecting the relative weakness of the  $CF_3I$  bond (53 kcal·mol<sup>-1</sup> for  $CF_3-I$ and 71 kcal·mol<sup>-1</sup> for CF<sub>3</sub>-Br).<sup>14</sup>

The rate constants for the association reactions involving Ga-(CH<sub>3</sub>)<sub>3</sub>, 1-C<sub>4</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> in Table I were measured under conditions where the rate of fsc collisions greatly exceeded the rate of reactive collisions. Thus the rate constants apply for equilibrated  $Ga(4^2P_J)$  concentrations, and therefore contain contributions from both k and k'. However, there is reason to expect that the inequality k' < k would hold, so that the observed rate constants essentially provide measurements of k; i.e., the k'contribution may be ignored. The reason for this is that an association complex involving Ga' as reactant would have an excess 826.2 cm<sup>-1</sup> or  $\simeq$  2.4 kcal·mol<sup>-1</sup> of energy over one involving Ga as reactant, and this could lead to a faster dissociation rate for the complex (larger value of  $k_{-2}$  in eq 5) and hence a slower reaction rate for Ga'.

3. Energetics of Association Reactions. The equilibrium constant  $K_p$  associated with equilibrium 1 may be written in terms of partition functions as

$$K_{\rm p} = \frac{p({\rm Ga})p({\rm Q})}{p({\rm Ga}{\rm Q})} = \frac{1}{N_0} \frac{(Z_{\rm Ga}^0)(Z_{\rm Q}^0)}{(Z_{\rm GaQ}^0)} \exp(-\Delta E_0/RT)$$
(7)

where  $Z^0$  represents the total partition function per molecule calculated relative to the ground-state energy for the standard condition of 1 atm pressure,  $N_0$  is Avogadro's number, and  $\Delta E_0$ is the energy in molar units required to dissociate the complex at 0 K. Values of  $K_p$  for complexes involving  $C_2H_4$ , 1- $C_4H_8$ , and Ga(CH<sub>3</sub>)<sub>3</sub>, obtained as the slopes of the plots shown in Figure 6, are given in Table III. The binding energy  $\Delta E_0$  may be obtained from the  $K_p$  value if estimates are available for the partition functions in eq 7.

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TABLE III: Estimation of Binding Energies for Ga Complexes<sup>4</sup>

complex	K <sub>p</sub> /atm	$(Z_1)N_0^{-1}/atm$	(Z <sub>2</sub> )	$\Delta E^{\circ}/$ (kcal· mol <sup>-1</sup> )
$Ga[C_2H_4]$	$8.2 \times 10^{-4}$	$3.6 \times 10^{6}$	$7 \times 10^{-4}$	9 ± 2
$Ga[1-C_4H_8]$	$5.2 \times 10^{-3}$	7.1 × 10^{6}	$4 \times 10^{-3}$	9 ± 2
$Ga[Ga(CH_3)_3]$	$2.2 \times 10^{-5}$	1.2 × 10^{7}	$5 \times 10^{-3}$	14 ± 2

"Headings are defined in the text.

Factorizing the partition functions into translational (t), rotational (r), vibrational (v), and electronic (e) parts, the expression for  $K_p$  may be written

$$K_{\rm p} = \frac{1}{N_0} (Z_1) (Z_2) \exp(-\Delta E_0 / RT)$$
(8)

where  $(Z_1)$  and  $(Z_2)$  are

$$(Z_1) = \frac{(Z_{Ga}^0)_t (Z_{Ga}^0)_e (Z_Q^0)_t (Z_Q^0)_e}{(Z_{GaQ}^0)_t (Z_{GaQ}^0)_e}$$
(9)

$$(Z_2) = \frac{(Z_Q^0)_r (Z_Q^0)_v}{(Z_{GaQ}^0)_r (Z_{GaQ}^0)_v}$$
(10)

The values of  $(Z_1)$  at 296 K for Q = C<sub>2</sub>H<sub>4</sub>, 1-C<sub>4</sub>H<sub>8</sub>, and Ga(CH<sub>3</sub>)<sub>3</sub> are obtained in a straightforward manner from standard expressions,<sup>16</sup> with the reasonable assumption  $(Z_{GaQ}^0)_e = 2$  in all cases. The results are given in Table III as values of  $(Z_1)/N_0$ .

The quantity  $(Z_2)$  is more difficult to evaluate because it depends on the vibrational/rotational energy level structure of the complex GaQ, which is not known. As a first approximation, treating the molecules as rigid structures with no internal rotations, the rotational parts may be estimated from the moments of inertia derived for assumed geometrical structures. This was done for  $Ga[C_2H_4]$  and  $Ga[1-C_4H_8]$  complexes with the Ga atom placed below the plane of the olefin and on a line normal to and bisecting the C=C bond. The Ga-C distance was taken to be 2.2 Å. The conformation of  $1-C_4H_8$  had all of the carbon atoms in a plane. For  $Ga[Ga(CH_3)_3]$  the attached Ga atom was placed below the planar GaC<sub>3</sub> skeleton, forming a Ga-Ga bond (2.5 Å) normal to the plane.

Considering now the vibrational component of  $(Z_2)$ , as a first approximation it may be assumed that all of the contributions from  $(Z_Q^0)_v$  due to the vibrational modes of Q are cancelled by the corresponding contributions in  $(Z_{GaQ}^{0})_{v}$  due to the vibrations of GaQ. This would leave only those contributions associated with the vibrational motion of Ga relative to Q in the GaQ complex, described by three vibrational frequencies. For all of the complexes considered, vibrational wavenumbers of 100, 50, and 50 cm<sup>-1</sup> were chosen to represent these modes. This selection leads to a vibrational component  $\simeq 0.02$  in  $(Z_2)$ . The values of  $(Z_2)$  estimated in this way are listed in Table III, together with the resulting values of the binding energy  $\Delta E_0$ .

The largest contribution by far to the preexponential factor in eq 8 is the quantity  $(Z_1)$ , which is known accurately. The much less accurately known quantity  $(Z_2)$  may be regarded as a relatively small correction to  $(Z_1)$ . As a consequence of the logarithmic relationship in eq 8, a rather large uncertainty in the product  $(Z_1)(Z_2)$  is reflected in a relatively small variation in the derived value of  $\Delta E_0$ . Thus for an error in  $(Z_2)$  corresponding to the range  $(Z_2) \times 0.01 - (Z_2) \times 100$ , the resulting error in  $\Delta E_0$ is  $\pm 2.7$  kcal-mol<sup>-1</sup> or  $\pm \approx 30\%$ . It is difficult to assess the absolute uncertainty connected with the estimation of  $(Z_2)$ , but by varying the assumed geometries and vibrational frequencies it was estimated that the uncertainty in the  $\Delta E_0$  values is  $\pm 2$  kcal·mol<sup>-1</sup>.

4. Nature of Ga Complexes. The occurrence of complex formation between neutral metal atoms and olefins has been observed for a number of metals including Al,<sup>6</sup> Cu,<sup>17</sup> Ag,<sup>17</sup> Ni,<sup>18</sup> Pd,<sup>18</sup> Sb,<sup>19</sup> and Bi.<sup>20</sup> Most relevant to the present study is the complex Al[ $C_2H_4$ ], which has been prepared under cryogenic conditions and characterized by ESR spectroscopy.<sup>6</sup> The ESR results point to a  $\pi$ -bonding arrangement involving delocalization of the electron in the singly occupied p-orbital of Al into the antibonding  $\pi^*$  orbital of C<sub>2</sub>H<sub>4</sub>. A similar bonding arrangement could account for the formation of Ga complexes with  $C_2H_4$  and  $1-C_4H_8$ , although alternative descriptions are possible including complexes involving Ga-C  $\sigma$ -bonds, for example, GaCH<sub>2</sub>-CH<sub>2</sub>. We favor the  $\pi$ -bonding description, primarily because of the analogy with  $Al[C_2H_4]$ ; the formation of a Ga-C but not a Al-C  $\sigma$ -bonded complex with C<sub>2</sub>H<sub>4</sub> is unlikely in view of the expected larger  $\sigma$ -bond energy in the case of Al.<sup>14</sup>

The binding energies for  $Ga[C_2H_4]$  and  $Ga[1-C_4H_8]$  in Table III (9  $\pm$  2 kcal·mol<sup>-1</sup>) may be compared with known metal-C<sub>2</sub>H<sub>4</sub> bond energies in stable transition-metal complexes:  $(C_2H_4)$ Fe-(CO)<sub>4</sub> (23.1 kcal·mol<sup>-1</sup>)<sup>21</sup> and (C<sub>2</sub>H<sub>4</sub>)Ni[ $(o-C_6H_5CH_3)_3PO_3$ ]<sub>2</sub> ( $\simeq$ 33 kcal·mol<sup>-1</sup>).<sup>22</sup> It is seen that the Ga-C<sub>2</sub>H<sub>4</sub> bond is relatively weak. Considering a  $\pi$ -complex description of the bonding, this may be understood in terms of two factors. Donation of electron density from the  $\pi$ -bond of C<sub>2</sub>H<sub>4</sub> to Ga is impeded by the absence of a low-lying, vacant acceptor orbital on Ga. The 3d and 4s orbitals are filled, so the acceptor function must involve the relatively high-energy 4p-orbital, likely in a hybrid combination with 4s. In the above Fe and Ni complexes there are vacant d-orbitals available for participation as hybridized acceptors for the  $\pi$ -electron density. Thus we would expect that the "forward donation" component of the metal-olefin bond would be relatively weak for Ga. This is consistent with the conclusion of Kasai<sup>6</sup> from ESR studies of  $Al[C_2H_4]$  that forward donation is probably insignificant for this complex. It may also be seen that "back donation" of electron density from the metal into the vacant  $\pi^*$ -antibonding orbital of C<sub>2</sub>H<sub>4</sub> may be expected to be relatively weak for Ga. This follows because in the simplest picture there is only one bonding electron available on Ga, occupying a 4porbital, whereas for the above Fe and Ni complexes there are doubly occupied d-orbitals available. These simple considerations provide a rationalization of the relative weakness of the  $Ga-C_2H_4$ bond.

In the experiments involving carbon monoxide and benzene as reactants with Ga there was no indication of complex formation. Thus Ga complexes with these molecules must be much more weakly bound than those involving  $C_2H_4$  or  $1-C_4H_8$ . It may be noted in this connection that the complexes  $Ga(CO)_2^4$  and Al- $(C_6H_6)^7$  have been isolated in cryogenic matrix deposits.

In the case of the reaction with  $C_2H_2$ , no evidence was found for the establishment of an equilibrium concentration of free Ga. This suggests that the  $Ga[C_2H_2]$  complex is significantly more strongly bound than  $Ga[C_2H_4]$  or  $Ga[1-C_4H_8]$ . The reaction of Al atoms with  $C_2H_2$ , in contrast to the case with  $C_2H_4$ , has been shown to produce a Al-C  $\sigma$ -bonded vinyl radical, AlCH=CH.<sup>6</sup> It is possible that a similar reaction occurs with Ga, the formation of a Ga–C  $\sigma$ -bond possibly accounting for the apparently greater binding energy compared with the Ga  $\pi$ -complexes with olefins.

It is worth noting that the termolecular rate constant for  $Ga/C_2H_2$  in Table I is nearly an order of magnitude larger than that for  $Ga/C_2H_4$ . This probably does not reflect a difference in activation energies, because both reactions proceeded at rates near the gas kinetic limit at sufficiently high Ar pressure, which implies very small activation barriers. In terms of the effective collision complex lifetimes  $\tau$  in Table I, the termolecular rate constants imply a longer lifetime for  $Ga[C_2H_2]$  (60 ps) than for  $Ga[C_2H_4]$  (7 ps), which is surprising in view of the somewhat

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smaller molecular size of  $Ga[C_2H_2]$ . Note that the  $\tau$  values for  $Ga[C_2H_4]$  (7 ps) and  $Ga[1-C_4H_8]$  (90 ps) in Table I follow the expected trend with molecular size. This trend is understandable in terms of a more rapid delocalization of energy and hence a longer lifetime with respect to unimolecular dissociation for collision complexes involving larger molecules. The large value of  $\tau$  for Ga[C<sub>2</sub>H<sub>2</sub>] compared with Ga[C<sub>2</sub>H<sub>4</sub>] may reflect the different nature of the complexes formed, involving disruption of the  $\sigma$ -bond framework in C<sub>2</sub>H<sub>2</sub> (forming Ga—CH=CH) but not in  $C_2H_4$  (forming a  $\pi$ -complex). This disruption could provide an efficient mechanism for delocalization of the excess energy of the collision complex throughout the molecule. It is possible that the origin of the apparently shorter lifetime for the  $C_2H_4$  case is in the availability of this delocalization mechanism for the Ga- $[C_2H_2]$  complex but not for the Ga $[C_2H_4]$  complex.

A surprising feature of the reaction of Ga with the perfluoroolefin  $C_2F_4$  is the observation of an Ar-pressure-independent reaction rate. In further contrast to the situation for the olefins  $C_2H_4$  and  $1-C_4H_8$ , there was no indication of an equilibration process indicative of complex formation. These observations, coupled with the relatively low value of the bimolecular rate constant, are suggestive of an abstraction mechanism for the reaction leading to GaF formation. This would be consistent with the tendency for halogen atom abstraction summarized in Tables I and II. Even considering that an abstraction channel may occur for the  $Ga/C_2F_4$  reaction, it is still somewhat surprising that complex formation apparently does not occur. The indication from this is that the binding energy of  $Ga[C_2F_4]$  is low relative to that of  $Ga[C_2H_4]$ .

In connection with the complex  $Ga[Ga(CH_3)_3]$ , it is interesting to note that the Ga binding energy  $14 \pm 2 \text{ kcal} \cdot \text{mol}^{-1}$  is roughly half of the bond energy of the gallium dimer Ga<sub>2</sub>,  $\simeq 32$  kcal $mol^{-1.23}$  In a simple picture of the bonding in Ga[Ga(CH<sub>3</sub>)<sub>3</sub>], the bond may be expected to occur between the singly occupied 4p-orbital of Ga and the lowest unoccupied molecular orbital of Ga(CH<sub>3</sub>)<sub>3</sub>, which is essentially a Ga 4p-orbital oriented perpendicular to the plane of the GaC<sub>3</sub> skeleton. In this picture the Ga 4s electrons form a nonbonding lone pair on Ga. The Ga-Ga  $\sigma$ -bond order is thus 1/2, which compares with the corresponding bond order for Ga<sub>2</sub> of 1. The approximately 2:1 ratio of the bond energies noted above is thus rationalized by this model.

In closing we note that the complexes described above should be amenable to low-temperature ESR studies of the type reported for Al[C<sub>2</sub>H<sub>2</sub>],<sup>6</sup> Al[C<sub>2</sub>H<sub>4</sub>],<sup>6</sup> and Ga(CO)<sub>2</sub>.<sup>4</sup> Such studies would be useful in assessing the simple bonding models suggested above.

Registry No. Ga, 7440-55-3; CF<sub>4</sub>, 75-73-0; CF<sub>3</sub>Cl, 75-72-9; CF<sub>3</sub>Br, 75-63-8; CF<sub>3</sub>I, 2314-97-8; SF<sub>6</sub>, 2551-62-4; C<sub>2</sub>F<sub>4</sub>, 116-14-3; N<sub>2</sub>O, 10024-97-2; C<sub>2</sub>H<sub>2</sub>, 74-86-2; C<sub>2</sub>H<sub>4</sub>, 74-85-1; 1-C<sub>4</sub>H<sub>8</sub>, 106-98-9; Ga(CH<sub>3</sub>)<sub>3</sub>, 1445-79-0.

# Theoretical Study of the Time Dependence of the Production of Excited N<sub>2</sub> by Subexcitation Electrons in Rare-Gas Mixtures<sup>1</sup>

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Experimental data are available which suggest that the fast production of electronic excited states in electron-irradiated helium- (or neon-) nitrogen mixtures is due to the interactions of subexcitation electrons. These systems-helium or neon with trace only amounts of  $N_2$ —lend themselves to theoretical analysis by various methods. Using only well-established cross-section data for inelastic and elastic processes in these systems allows the time dependence of the evolution of emission from the  $C^3\Pi_u$  state of  $N_2$  to be calculated. The results of these calculations show (i) support for the subexcitation electron mechanism; (ii) that the continuous slowing down approximation is inappropriate in these systems; (iii) that a Monte-Carlo technique gives satisfactory agreement between theory and experiment; and (iv) that more reliable data and a closer analysis of it will assist further development of these ideas.

#### Introduction

Recent experimental work by Cooper, Denison, and Sauer<sup>2</sup> has reported the use of pulse radiolysis to study the kinetics of formation and decay of the excited states in electron-irradiated rare gas-trace-nitrogen gas mixtures.

The formation and radiative decay of the  $C^3\Pi_u$  state of N<sub>2</sub> was monitored by observing the intensity of emission at 379 nm. The kinetics and intensity of  $N_2$  emission were dependent on  $N_2$ pressure. These emission kinetics were monitored during a time domain short compared to that necessary for energy transfer or ion recombination processes to be important. The authors conclude that the excitation of  $N_2$  is due to the energy degradation of subexcitation electrons, i.e., electrons of energy less than the lowest excited level of He (19.8 eV) or Ne (16.6 eV), but sufficient to excite the  $C^{3}\Pi_{u}$  state of N<sub>2</sub> (11.15 eV). The energy loss processes

for these electrons are the following:

$$\mathbf{e}^- + \mathbf{N}_2 \to \mathbf{e}^- + \mathbf{N}_2^* \tag{1}$$

$$e^{-} + N_2 \rightarrow e^{-} + N_2^{+} + e^{-}$$
 (2)

$$e^- + He \text{ (or Ne)} \rightarrow e^- + He \text{ (or Ne)}$$
 (3)

Process 1 is the electronic excitation of the nitrogen molecule, and the minimum threshold energy is about 6 eV. Depending upon the excited state produced, the cross section has different energy dependence and different energy losses. We shall consider ten major excited states relevant in the energy range of interest, which is below 19.8 eV in He and below 16.6 eV in Ne. Process 2 is the ionization, and the minimum threshold energy is 15.6 eV. Process 3 is the elastic scattering by He or Ne and the energy

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