TABLE VI: Fitting Parameters for Simulated Anisotropic ORDB **Fluorescence Profiles** 

$$I_{\parallel,\perp} = P(t)[1 \pm 0.5r(t) \ G^{s}(t)]$$

 $G^{s}(t) = \exp[-1.354C(t/4\tau)^{1/3}]$ 

 CD	0.886C <sub>D</sub> <sup>a</sup>	Δ, %	$\chi_{\Gamma}^{2}(\parallel), \chi_{\Gamma}^{2}(\perp)$
 0.178	0.140	-11.2	1.15, 1.06
0.316	0.236	-15.7	0.992, 0.982
0.562	0.433	-13.2	1.11, 1.01
1.00	0.755	-14.9	1.18, 1.14
1.78	1.33	-15.6	1.28, 1.21
3.16	2.41	-14.1	1.28, 1.08
5.62	4.47	-10.4	1.06, 1.18

<sup>a</sup>Static orientational factor for two-dimensional system with moments randomly distributed on cone with  $\theta^* = 58.4^{\circ}$ .

 $\sim$ 15% in the deconvolutions. Moreover, the percent discrepancies  $\Delta$  are nearly constant, and the linearity of a plot similar to that in Figure 5 is hardly affected. Hence, our conclusion that the two-dimensional two-particle theory for  $G^{s}(t)$  works well for all of the densities shown in Figure 5 is not sensitive to the model assumed for the orientational distribution of transition moments.

Polarized fluorescence profiles obtained at higher chromophore densities than those shown in Table I show an interesting anomaly in that the fluorescence components  $I_{\parallel}$ ,  $I_{\perp}$  do not converge together at long times. At  $1511 \times 10^{-6}$  chromophores/Å<sup>2</sup>, the two profiles intersect after  $\sim 1$  ns, and  $I_{\perp}$  decays more slowly than  $I_{\parallel}$  at long times. At 2932 × 10<sup>-6</sup> chromophores/Å<sup>2</sup>,  $I_{\perp}$  remains below  $I_{\parallel}$ at all times, and the phenomenological decay times are markedly reduced. These ODRB densities are extremely large (the latter density corresponds to packing and average of  $\sim 16$  chromophores per circle of radius  $R_0 = 44.7$  Å), and these polarization effects may result from excimer formation.

We showed earlier<sup>8</sup> that the three-dimensional two-particle theory of Huber et al.<sup>1</sup> furnishes an accurate description of transport in solution for reduced concentrations up to  $\sim 3$  in the absence of orientational correlation. Figure 5 indicates that the two-dimensional analogue (eq 3) of the Huber theory is valid for reduced ODRB densities  $C_D$  up to ~5. This result is of particular interest, because density expansions of  $G^{s}(t)$  converge more slowly in systems of lower dimensionality. Hence, one may expect the demonstrated validity of the two-particle theory to be exhibited a fortieri in random three-dimensional systems; the system dimensionality does not pose fundamental problems in our understanding of singlet excitation transport.

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# Vibrational and Electronic Spectra of Matrix-Isolated N<sub>3</sub>• and N<sub>3</sub><sup>-</sup>

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 $N_3$  and  $N_3$  were formed upon the bombardment of a  $N_2$  matrix with kiloelectronvolt-energy fast atoms and/or ions. The vibrational frequencies of N<sub>3</sub> in the most stable site,  $\nu_2 = 472.7$ ,  $\nu_3 = 1657.5$ , and  $\nu_1 + \nu_3 = 2944.9$  cm<sup>-1</sup>, as well as those in two other sites were obtained, and dissociation into N(<sup>2</sup>D) and N<sub>2</sub>(<sup>1</sup> $\Sigma_g^+$ ) was observed upon <sup>2</sup> $\Sigma_u^+ \leftarrow {}^2\Pi_g$  excitation of N<sub>3</sub> at 272 nm. The  $\nu_3$  vibrational frequencies of free and ion-paired N<sub>3</sub><sup>-1</sup> in a nitrogen matrix are 2003.5 and 2077.8 cm<sup>-1</sup>, and their photodetachment thresholds in a mixed nitrogen-argon matrix ( $\sim 2:1$ ) are 4.5 and 3.4 eV, respectively. The experimental frequencies are compared with the results of Hartree-Fock computations for  $N_3$  and  $N_3$ . The results of similar computations for  $N_3^+$  agree with an extrapolation of the experimental frequencies from  $N_3^-$  and  $N_3^-$  and suggest strongly a value near 1200 cm<sup>-1</sup> for  $\nu_3$ .

### Introduction

Low-temperature matrix deposition with simultaneous fast atom<sup>2</sup> and/or fast ion<sup>3</sup> bombardment offers access to spectroscopic concentrations of highly reactive molecules by using readily available stable precursors. We have discovered that the deposition of nitrogen gas on a gold surface while bombarding with 4-6-keV Ne or Ar atoms and/or ions yields strong spectra of the  $N_3$  radical along with weak lines due to the N3<sup>-</sup> anion and have used the technique to investigate IR absorption of both species, the UVvisible absorption and emission of the former, and photodetachment of the latter, isolated in a neat nitrogen or a mixed nitrogen-argon matrix.

The N<sub>3</sub> radical was first observed in the gas phase and characterized by a 272-nm absorption band in the UV region.<sup>4</sup>

At shorter wavelengths, the spectrum was diffuse, and therefore predissociation from the upper state was suspected. An analysis of the rotational fine structure<sup>5</sup> permitted a  ${}^{2}\Sigma_{u}^{+} \leftarrow {}^{2}\Pi_{g}$  assignment of the observed transition and showed that in the ground  ${}^{2}\Pi_{a}$  state the molecule is of  $D_{\infty h}$  symmetry, with bond lengths equal to 1.181 Å. The electronic ground-state spin-orbit splitting was determined to be 81 cm<sup>-1</sup>, and the Renner-Teller structure in the absorption of N<sub>3</sub> containing a quantum of the bending vibration was identified tentatively. In megaelectronvolt-electron or UV-photon irradiated dilute aqueous solution of sodium azide ( $\sim 10^{-4}$  M), the  $N_3$  absorption band maximum has been reported variously at 278,<sup>6</sup> 277<sup>7</sup> and 272<sup>8</sup> nm. The photoelectron spectrum of  $N_3$ . is compatible with the  ${}^{2}\Pi_{g}$  ground state, and the first ionization potential is 11.06 eV.<sup>9</sup>

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Little is known about the vibrations of  $N_3$ . The antisymmetric stretch  $v_3$  has been assigned at 1700 cm<sup>-1</sup> in the  ${}^{2}\Sigma_{u}^{+}$  excited state<sup>4</sup> and at 2150 cm<sup>-1</sup> in the  ${}^{2}\Pi_{g}$  ground state.<sup>10</sup> As we will show, the latter assignment needs to be revised.

Very recently, a gas-phase study of laser-induced fluorescence of N<sub>3</sub> appeared.<sup>11</sup> It confirmed the Renner-Teller structure, established the  ${}^{2}\Sigma_{\mu}^{+}$  lifetime as less than 20 ns, and reported weak vibrational structure from which  $\omega_1 = 1320 \pm 50 \text{ cm}^{-1}$  and  $\omega_2 =$  $457 \pm 25 \text{ cm}^{-1}$  were deduced. As we shall see, these results are in excellent agreement with our matrix-isolation results.

The  $N_3^-$  anion has been the subject of much more attention by spectroscopists. A tremendous amount of work has been done in the solid phase: in single crystals, in polycrystalline materials, and in KBr pellets. Most of this work was done by physicists interested in matters such as the dynamics of the phonon vibrations, the crystal field, or the electronic band structure. The vibrational frequencies of N<sub>3</sub><sup>-</sup> vary slightly from one metal azide to another. In solid KN<sub>3</sub>, they are 1344  $(v_1)$ , 642.2  $(v_2)$ , and 2036.4 cm<sup>-1</sup> ( $\nu_3$ ).<sup>12</sup> The  $\nu_1$  frequency of N<sub>3</sub><sup>-</sup> in infinitely dilute aqueous solution was obtained by Raman spectroscopy at 1342.7 cm<sup>-1</sup> by extrapolation from solutions of different concentrations of alkali-metal azides.<sup>13</sup> The vibrational frequencies for the isotopomers,  $^{14}N_3^{-}$ ,  $^{14}N^{14}N^{15}N^{-}$ ,  $^{14}N^{15}N^{14}N^{-}$ , and  $^{15}N_3^{-}$  in KBr lattice are  $\nu_3$ 2037.1, 2025.0, 1991.0, and 1968.3 cm<sup>-1</sup>, respectively, and  $\nu_2$  640.1, 636.5, 625.7, and 618.3 cm<sup>-1</sup>, respectively.<sup>14</sup> The UV spectrum measured on solid films of alkali azides showed an absorption band attributable to  $N_3^-$  at 222.5 nm.<sup>15</sup> Several additional spectroscopic studies of the  $N_3^-$  anion in solutions have appeared. Two UV absorptions at 230 and 180 nm were assigned to  ${}^{1}\Delta_{u} \leftarrow {}^{1}\Sigma_{g}^{+}$  and  ${}^{1}\Sigma_{u}^{+} \leftarrow {}^{1}\Sigma_{g}^{+}$  transitions, respectively.<sup>16</sup> The reversed assignment has been proposed as well, based on the comparison with UV spectra of HN<sub>3</sub> and solid films of alkali azides,<sup>17</sup> and is supported by quantum chemical computations.<sup>18</sup> The photoelectron spectrum of  $N_3^-$  in solution was also reported.<sup>19</sup> In the gas phase,  $N_3$  has bond lengths of 1.1884 Å, and the antisymmetric stretch lies at  $\nu_3 = 1986.4672$  cm<sup>-1.20</sup> Its photodetachment threshold lies at 449 nm and corresponds to an N<sub>3</sub> electron affinity of 2.76 eV.21

## **Experimental Section**

The apparatus<sup>22</sup> consisted of a miniature fast atom capillaritron source (FACS) (Phrasor Scientific Inc.), directed at a CsI window cooled to about 20 K by a closed-cycle cryostat (Air Products Displex), and of an inlet for nitrogen (Airco, 99.999% purity). The fast atom gun chamber and the top of the cryostat shroud were pumped by two 2-in. diffusion pumps. The bombarding gas was neon (Airco, 99.999% purity) or argon (Airco, 99.999% purity). While there was no evidence that neon condenses in the matrix, argon codeposits with  $N_2$  readily so that a mixed matrix results.

Typical experimental conditions involved a mixture of fast Ne and Ne<sup>+</sup> produced by the FACS as the bombarding particles at

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4 keV and ion current reading of 80  $\mu$ A, 6 mmol/h N<sub>2</sub> deposition for optimal IR results, and 3 mM/h for optimal UV-visible results. The deposition time was 0.5-6 h, with chamber pressure of the order of  $10^{-3}$  Torr. Before a N<sub>2</sub> deposition was started, the gun was run at a beam current of 300  $\mu$ A at 5 keV for 5 h to remove CO<sub>2</sub> adsorbed on the surface of the chamber. When this precaution was not taken, peaks due to CO<sub>2</sub> and CO as well as other contaminants produced therefrom appeared in the IR spectra. Each time before bombardment, a protective layer of  $N_2$  was deposited onto the window. Painstaking attention was paid to the exclusion of water.

Spectra were measured on a Nicolet 6000 FT-IR spectrometer, a Cary 17D UV-visible spectrometer, an IBM-Brucker ER 200 ESR spectrometer, and a home-built spectrofluorimeter with a Spex 0.5-m double and a Spex 0.75-m single monochromator for excitation and emission, respectively, with a 1-kW xenon arc lamp and a Centronix Series 4283 Model S-20 response cooled photomultiplier running at 1 keV with a Spex PC photon counter. When needed, Glan polarizers were placed immediately before and after the matrix along the paths of emission and excitation light. An IBM IR 98 FT-IR spectrometer with a  $3-\mu m$  Mylar beam splitter and a deuteriated triglycine sulfate detector was also used for some of the IR measurements.

In some experiments, a filament of a 12-V light bulb was mounted in front of the cold window on the matrix side and about an inch away from it. The positive side of the power supply was connected to the instrument ground so that the negative potential on the filament repels the hot electrons toward the matrix. The temperature of the filament was variable from hot to glowing white by changing the voltage of the power supply.

The irradiations were done through a quartz window with a low-pressure Hg lamp whose 254-nm output is in the milliwatt region, a portable ellipsoidal xenon arc lamp (Cermax 300W) with a water filter in front to eliminate IR light, and a dye laser (Lumonics, HyperDye-300) pumped by an excimer laser (Lumonics, HyperEx-400) and doubled with a frequency-doubling crystal. The doubled-frequency laser light was linearly polarized, and the fundamental line was blocked out by a UV-transmitting visible-cutoff filter. UV and visible cutoff filters were used in conjunction with the portable xenon arc lamp to obtain light with a known short-wavelength cutoff in determining the photodetachment threshold.

Restricted  $(N_3^{-})$  and unrestricted  $(N_3, N_3^{+})$  self-consistent field (SCF) computations were done with the GAUSSIAN-80 UCSF program<sup>23</sup> with standard 4-31G\* and 6-311G\* basis sets.

### Results

General. The observed spectra were independent of the precise experimental conditions such as the fast particle energy. They were the same whether only fast atoms or a fast atom-fast ion mixture was used for the bombardment. The presence of  $N(^{4}S)$ atoms in the neon-bombarded nitrogen matrix was obvious from their sharp ESR signals, and the presence of N<sub>3</sub>, was indicated by the appearance of a sharp absorption peak at 272 nm  $[^{2}\Sigma_{u}]$  $- {}^{2}\Pi_{g}$ ). Excitation at 272 nm produced a strong phosphorescence peak at 524 nm with a lifetime of  $31 \pm 1.4$  s (N,  $^{2}D \rightarrow ^{4}S$ ), and a weak one at 595 nm with a lifetime of 29  $\pm$  1.7 s [N + N<sub>2</sub>, <sup>2</sup>D +  ${}^{1}\Sigma_{g}^{+}(v=0) \rightarrow {}^{4}S + {}^{1}\Sigma_{g}^{+}(v=1)].{}^{24,25}$  If N<sub>3</sub> fluorescence peaks near 279 and 282 nm (gas-phase values<sup>11</sup>) were present, they were orders of magnitude weaker than the phosphorescence and were not observed. The phosphorescence at 524 nm was completely depolarized even when the 272-nm exciting light was linearly polarized. The 595-nm emission line was too weak for a reliable measurement of polarization ratio. The excitation spectra monitored at either wavelength were identical with each other and with the observed UV absorption spectrum (a peak at 272 nm). The lifetimes obtained in our experiments at 20 K were somewhat

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Figure 1. Base-line-corrected FT-IR spectrum of  ${}^{14}N_2$  bombarded with 4-keV Ne and Ne<sup>+</sup> (80  $\mu$ A). Details of parts A-D are shown in Figure 2. Deposition rate: 6 mmol/h at 20 K. The crossed peaks are not reproducible and are due to noise or impurities. CO<sub>2</sub>, 2349.3 cm<sup>-1</sup>;  ${}^{14}N_2$ , 2328.2 cm<sup>-1</sup>; N<sub>2</sub>O, 2236.9 cm<sup>-1</sup>; CO, 2139.2 cm<sup>-1</sup>; NO, 1874.9 cm<sup>-1</sup>; H<sub>2</sub>O, 1597.0 cm<sup>-1</sup>.

shorter than those reported for these two emissions at 4 K [for both lines, 42 s in one case (condensation of products from electrical discharge of N<sub>2</sub> gas, electron bombardment of solid N<sub>2</sub>, and warmup of these matrices, as well as warmup of a  $\gamma$ -rayirradiated matrix)<sup>24</sup> and 37 s in another (pulsed keV electron bombardment of solid N<sub>2</sub>)<sup>25</sup>].

After an extended period of irradiation at 272 nm, a decrease in the N<sub>3</sub> absorption and emission intensities was noticeable. After the total disappearance of the absorption peak, the ESR intensity of N(<sup>4</sup>S) signals exceeded by about 6% the level present after the initial bombardment. These observations are compatible with photoinduced dissociation of excited N<sub>3</sub> ( ${}^{2}\Sigma_{u}^{+}$ ) into N(<sup>2</sup>D) and N<sub>2</sub>( ${}^{1}\Sigma_{g}^{+}$ ). An observable ESR signal is not expected for the orbitally degenerate N<sub>3</sub> radical.

When  ${}^{15}N_2$  was used in place of  ${}^{14}N_2$ , the 272- and 524-nm peaks did not change their position, but the 595-nm phosphorescence peak shifted to 592.5  $\pm$  0.25 nm, in good agreement with the value of 292.25 nm expected from the difference in ground-state vibrational frequencies of solid  ${}^{15}N_2$  (2250.2 cm<sup>-1</sup>) and  ${}^{14}N_2$  (2328.2 cm<sup>-1</sup>) observed in our IR measurements.

The IR spectrum (Figures 1 and 2) of the same bombarded matrices contained intense peaks at 1657.5 and 1652.6 cm<sup>-1</sup> and weak peaks at 2944.9, 2939.2, 2935.6, 2077.8, 2003.5, 1654.5, 474.9, and 472.7 cm<sup>-1</sup>. The 474.9-cm<sup>-1</sup> peak is hard to distinguish from noise but is reproducible. In the spectrum shown on the right-hand side of Figure 2A, this peak is not present because a higher deposition temperature was used to get a matrix of better quality. Weak peaks attributable to the matrix itself and to CO<sub>2</sub>, CO, and H<sub>2</sub>O contaminants were usually also present to a variable degree as were other contaminants attributable to products originating in the fragmentation of CO<sub>2</sub>. When Ar was used as bombarding gas, i.e., in a mixed nitrogen-argon matrix, the frequencies shifted slightly, the peaks were somewhat broader, and the relative intensity of 2003.5-cm<sup>-1</sup> peak increased strikingly relative to the rest of the peaks.

Bleaching experiments showed that all these IR peaks belong to two different species. Those at 2944.9, 2939.2, 2935.6, 1657.5, 1654.5, 1652.6, 474.9, and 472.7 cm<sup>-1</sup> (group I) gradually disappeared over about a 5-h period of irradiation with a low-pressure Hg lamp, whose main output line is at 254 nm, while those at 2077.8 and 2003.5 cm<sup>-1</sup> (group II) disappeared much faster, in about 4 min. On the other hand, irradiation with a beam of 272-nm laser light caused the peaks of group I to disappear faster than those of group II. Within each group, all IR peaks retained their relative intensities during the bleaching process, suggesting that only two distinct chemical species were being observed in the IR spectra. The dependence on the wavelength of the bleaching light suggests that the IR peaks of group I are due to the carrier of the 272-nm absorption in the UV, i.e., to N<sub>3</sub>, whereas those of group II must be due to a species without a structured UVvisible absorption band, unnoticed in our UV-visible spectra. Combined IR-UV measurements on the same matrix during a bleaching with the low-pressure Hg lamp indeed showed that the UV-visible absorption spectrum was not affected detectably upon a total disappearance of the IR peaks of group II, and that the intensity of the 272-nm absorption in the UV was proportional to those of the IR peaks of group I.

The Azide Radical,  $N_3$ . The identity of the carrier of group I peaks with the carrier of the 272-nm peak and, thus, with  $N_{3}$ , was confirmed by a photoselection experiment in which a beam of 272-nm laser light linearly polarized along the laboratory Zaxis was used for partial bleaching. This induced linear dichroism  $(d = E_Z/E_Y)$  in the remaining group I IR peaks  $(d_{2944.9} = d_{1657.5})$ =  $1.10 \pm 0.03$ ,  $d_{472.7} = 0.911 \pm 0.04$ ) but not in group II IR peaks. Converted to the orientation factors  $K_i$  for the transition moment direction  $[K_i = \langle \cos^2 \tilde{j} \rangle = d_i / (d_i + 2)$ , where  $\tilde{j}$  is the angle between the *j*th transition moment and Z, and the angular brackets indicate averaging over the sample],<sup>26</sup> this yields  $K_{2944.9} = K_{1657.5} = 0.355 \pm 0.013$  and  $K_{472.7} = 0.313 \pm 0.018$ . The 272-nm electronic transition moment of  $N_{3}$ , is perpendicular to the molecular axis z.<sup>5</sup> The sign of the observed dichroism thus shows that the transition moments of the IR transitions at 2944.9 and 1657.5 cm<sup>-1</sup> lie along the molecular axis, as expected for the  $v_1 + v_3$  and  $v_3$  stretching vibrations, and that the moment of the 472.7-cm<sup>-1</sup> transition is perpendicular to the molecular axis, as expected for the  $\nu_2$  bend. From the symmetry of the molecule,  $K_x = K_y = K_{472.7}$ = 0.313 ± 0.018 and  $K_z = K_{2944.9} = K_{1657.5} = 0.355 \pm 0.013$ .  $K_x$  $+ K_v + K_z = 0.98 \pm 0.05$ , within our experimental error of the theoretical value of unity. The peak at 1652.6 cm<sup>-1</sup> showed the same dichroic ratio as the peak at 1657.5 cm<sup>-1</sup> in a separate measurement, but the other peaks of group I were too weak for

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TABLE I:	Vibrational	Frequencies	(cm <sup>-1</sup> )	and Intensity	y Ratios of N	3 Isotopome
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		exptl	calcd <sup>a</sup>	compd <sup>b</sup>	$I(\nu_1 + \nu_3)/I(\nu_3)^c$
14N14N14N	$\nu_1 + \nu_3$	2944.9		3170.1 (2944.9)	$4.7 \times 10^{-2} \ (\pm 2\%)$
	$\nu_2$	472.7		600.9 (472.7)	
	<i>v</i> <sub>3</sub>	1657.5		1674.9 (1657.5)	
$^{14}N^{14}N^{15$	$\nu_1 + \nu_3$	2917.1	2914.1	3134.8 (2912.1)	$3.4 \times 10^{-2} \ (\pm 10\%)$
	$\nu_2$		470.1	597.5 (470.0)	
	$\nu_3$	1649.3	1648.3	1665.6 (1648.3)	
<sup>15</sup> N <sup>14</sup> N <sup>15</sup> N <sup>.</sup>	$v_1 + v_3$	2890 <sup>d</sup>	2882.9	3100.9 (2880.6)	$1.7 \times 10^{-2} \ (\pm 100\%)$
	$\nu_2$		467.4	594.2 (467.4)	
	$\nu_3$	1639.7	1639.0	1656.2 (1639.0)	
$^{14}N^{15}N^{14}N^{.}$	$v_1 + v_3$	2907.2	2907.8	3132.6 (2910.1)	$6.5 \times 10^{-2} \ (\pm 10\%)$
	$\nu_2$		462.1	587.4 (462.1)	
	$\nu_3$	1621.4	1620.4	1637.5 (1620.5)	
<sup>14</sup> N <sup>15</sup> N <sup>15</sup> N <sup>.</sup>	$\nu_1 + \nu_3$	2878.4	2876.7	3098.6 (2878.5)	$5.8 \times 10^{-2} \ (\pm 10\%)$
	$\nu_2$		459.4	584.0 (459.4)	
	<i>v</i> <sub>3</sub>	1612.7	1610.9	1630.8 (1613.9)	
<sup>15</sup> N <sup>15</sup> N <sup>15</sup> N <sup>.</sup>	$\nu_1 + \nu_3$	2848.5	2845.4	3062.9 (2845.3)	$4.2 \times 10^{-2} \ (\pm 50\%)$
	$\nu_2$	457.1	456.7	580.5 (456.7)	
	$\nu_3$	1603.2	1601.5	1618.3 (1601.5)	

<sup>a</sup>Calculated from the frequencies of <sup>14</sup>N<sub>3</sub> by using the formulas given by Herzberg.<sup>27</sup> <sup>b</sup>UHF computation using the 6-311G\* basis set combined with the FG matrix method. The numbers in parentheses are obtained by multiplication with common factors 0.928 84 for  $\nu_1 + \nu_3$ , 0.78665 for  $\nu_2$ , and 0.989 49 for  $\nu_3$ , chosen so that the frequencies for <sup>14</sup>N<sub>3</sub> agree with the experimental values. For the bending vibration, the average of the two computed frequencies was used, and spin-orbit coupling and Renner-Teller effects were not considered. <sup>c</sup>Observed integrated intensity ratio. The value for <sup>14</sup>N<sub>3</sub> was obtained with <sup>14</sup>N<sub>2</sub>, and that for <sup>15</sup>N<sub>3</sub> was obtained with <sup>15</sup>N<sub>2</sub>. The others were obtained with <sup>14</sup>N<sup>15</sup>N. <sup>d</sup> The peak is weak, and its frequency deviates significantly from the calculations. See Figure 5.



Figure 2. Details of parts A-D in Figure 1. The spectrum shown on the right side of A was obtained in a separate experiment at 30 K with an IBM FT-IR spectrometer.

the determination of their dichroic ratio.

The appearance of three closely spaced IR peaks near 2940  $cm^{-1}$ , of three near 1655  $cm^{-1}$ , and of two near 472  $cm^{-1}$ , in place of the expected single peaks, is due to site effects: (1) When the deposition rate was reduced a few times below that normally used

or when the temperature of the cold window during the deposition was about 10 K higher, only the peaks at 2944.9 and 1657.5 cm<sup>-1</sup> appeared, and an increase in the deposition rate enhanced the intensity of the other four IR peaks relative to the 2944.9- and 1657.5-cm<sup>-1</sup> peaks. (2) When a matrix exhibiting three IR peaks near 2940 cm<sup>-1</sup> and three near 1655 cm<sup>-1</sup> was repeatedly annealed by warming up a few degrees and then recooling, the peaks at 2944.9 and 1657.5  $\text{cm}^{-1}$  gradually increased while those at 2939.2, 2935.6, 1654.5, and 1652.6  $cm^{-1}$  decreased and eventually disappeared altogether. In this process, the sum of the integrated intensities of the three peaks at 1657.5, 1654.5, and 1652.6 cm<sup>-1</sup> decreased by about 7%, while the IR peak due to a small amount of CO used as internal standard did not change, suggesting that either some of the N<sub>3</sub>, is destroyed in the annealing process or that the  $N_3$  species at three different sites have slightly different transition moments, with the most stable site showing the weakest absorption. Further, (3) all three IR peaks near 1655 cm<sup>-1</sup> showed identical isotopic shifts for all isotopomers. Vibrations of the isotopomers in the unstable sites were not observable near 2940 cm<sup>-1</sup> because of their low IR intensities. Finally, (4) at these temperatures, the  ${}^{2}\Pi_{1/2}$  state of N<sub>3</sub> is not expected to have an observable population, since it lies  $\sim 71~\text{cm}^{-1}$  above the  $^2\Pi_{3/2}$ ground state.5

We conclude that the ground-state N<sub>3</sub>· radical contained in the most stable site in solid N<sub>2</sub> has a strong IR peak at 1657.5 cm<sup>-1</sup> ( $\nu_3$ ) and weak IR peaks at 2944.9 ( $\nu_1 + \nu_3$ ) and 472.7 cm<sup>-1</sup> ( $\nu_2$ ).

Similar IR measurements in which  ${}^{14}N_2$  was replaced by  ${}^{15}N_2$  (Figures 3 and 4),  ${}^{14}N^{15}N$  (Figure 5), or mixtures of  ${}^{14}N_2$  and  ${}^{15}N_2$  permitted the assignment of isotopic shifts<sup>27</sup> (Table I). The results from the mixtures of  ${}^{14}N_2$  and  ${}^{15}N_2$  experiments are consistent with those in other isotopic experiments.

The relative integrated intensities of isotopically shifted 2944.9and 1657.5-cm<sup>-1</sup> peaks vary as a function of the isotopic substitutions (Table I). The data on  ${}^{14}N^{15}N$ ·,  ${}^{15}N^{14}N^{15}N$ ·,  ${}^{14}N^{15}N^{14}N$ ·, and  ${}^{14}N^{15}N$ · were obtained in a single experiment. The information on  ${}^{14}N_3$ · was obtained in a separate experiment, and so was that on  ${}^{15}N_3$ ·.

Much effort was put into searching for the other three vibrational transitions expected in principle from the spin-orbit coupling and Renner-Teller effects, but no other peaks were observed above the noise level at frequencies higher than  $430 \text{ cm}^{-1}$ .

The Azide Anion,  $N_3^-$ . The identity of the group II IR peaks at 2077.8 and 2003.5 cm<sup>-1</sup> was more difficult to establish since

<sup>(27)</sup> Herzberg, G. Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules; Van Nostrand: New York, 1945; pp 172-173 and p 187.



Figure 3. Base-line-corrected FT-IR spectrum of  ${}^{15}N_2$  bombarded with 4-keV Ne and Ne<sup>+</sup> (80  $\mu$ A). Details of parts A–D are shown in Figure 4. Deposition rate: 6 mmol/h at 20 K. The spectrum was obtained by subtracting the single-beam spectra before irradiation and after irradiation with a lamp. The negative peaks are due to this operation. The crossed peaks are not reproducible and are due to noise or impurities.  ${}^{15}N_2$ , 2250.2 cm<sup>-1</sup>; CO, 2139.5 cm<sup>-1</sup>;  ${}^{15}N_2$ , 1581.4 cm<sup>-1</sup>.



Figure 4. Details of parts A-D in Figure 3.

they were not associated with any obvious features in the UV absorption spectrum and since they were so weak.



**Figure 5.**  $\nu_3$  and  $\nu_1 + \nu_3$  vibrational frequencies of four of the six isotopomers of azido radical N<sub>3</sub> obtained by the bombardment of <sup>14</sup>N<sup>15</sup>N with 4 keV Ne and Ne<sup>+</sup> (80  $\mu$ A). Deposition rate: 3 mmol/h at 20 K. The spectrum was obtained by subtracting the single-beam spectra before irradiation and after irradiation with a lamp. The negative peaks are due to this operation. The crossed peaks are not reproducible and are due to impurities.

The diffuse nature of the UV-visible absorption spectrum of this species, its high sensitivity to bleaching with UV light, and the absence of detectable emission are all compatible with its assignment as an anion. We believe that the two IR peaks are both due to  $N_3^-$  but in different environments, on the basis of the following evidence: (1) The intensity of the 2077.8-cm<sup>-1</sup> peak relative to that of the 2003.5-cm<sup>-1</sup> peak was small at lower  $N_2$ 

TABLE II: Antisymmetric Vibrational Frequencies  $\nu_3$  of Isotopomers of Free N<sub>3</sub><sup>-</sup> (cm<sup>-1</sup>)

	<sup>14</sup> N <sup>14</sup> N <sup>14</sup> N <sup>-</sup>	<sup>14</sup> N <sup>14</sup> N <sup>15</sup> N <sup>-</sup>	<sup>15</sup> N <sup>14</sup> N <sup>15</sup> N <sup>-</sup>	<sup>14</sup> N <sup>15</sup> N <sup>14</sup> N <sup>-</sup>	<sup>14</sup> N <sup>15</sup> N <sup>15</sup> N <sup>-</sup>	<sup>15</sup> N <sup>15</sup> N <sup>15</sup> N <sup>-</sup>
exptl	2003.5	1993.0	1982.1	1959.9	1949.0	1937.7
calcd <sup>a</sup>		1992.4	1981.2	1958.6	1947.2	1935.8
compd <sup>b</sup>	2266.3	2253.6	2241.0	2215.5	2203.5	2189.6
corr <sup>c</sup>	2003.5	1992.3	1981.1	1958.6	1948.0	1935.7

<sup>a</sup>Calculated from the frequencies of <sup>14</sup>N<sub>3</sub><sup>-</sup> by using the formulas given by Herzberg.<sup>27</sup> <sup>b</sup>RHF computation using the 6-311G\* basis set combined with the FG matrix method. <sup>c</sup>Obtained by multiplication of the computed values with a common factor 0.88404 chosen so that the  $\nu_3$  frequency for <sup>14</sup>N<sub>3</sub><sup>-</sup> agrees with the experimental value.

deposition rate, reached a maximum at a deposition rate equal to about half of that normally used, and then decreased as the deposition rate was increased further. (2) Dilution of nitrogen by argon enhanced the intensity of the lower frequency peak significantly. (3) When the matrix was annealed, the 2003.5-cm<sup>-1</sup> peak decreased, the 2077.8-cm<sup>-1</sup> peak increased, and the sum of their integrated intensities decreased by about 7%, judging by a CO internal standard. These changes occurred at annealing temperatures about 10 K higher than the analogous site annealing observed for the IR peaks of the N<sub>3</sub> radical. Indeed, before the 2003.5-cm<sup>-1</sup> peak disappeared altogether, the matrix invariably evaporated. In keeping with the requirement for a relatively high annealing temperature, the 2077.8/2003.5 intensity ratio remained unaffected by a 10 K increase in the temperature of the deposition window during matrix deposition.

The relative difficulty with which the 2003.5-cm<sup>-1</sup> peak converts into the 2077.8-cm<sup>-1</sup> peak suggests that the process may involve more than a mere rearrangement of the N<sub>2</sub> molecules in the environment, as is presumably the case in the annealing of the sites of the neutral N<sub>3</sub> species. Instead, we suspect that actual diffusion of a counterion to the proximity of the anion is responsible. The 2003.5-cm<sup>-1</sup> peak might be due to a free anion and the 2077.8-cm<sup>-1</sup> peak due to an "ion pair". This assignment is compatible with the gas-phase frequency of 1986.5 cm<sup>-1</sup>,<sup>20</sup> the 2037-cm<sup>-1</sup> frequency in a KBr lattice,<sup>14</sup> and the known differences in the frequencies of free and ion-paired anions.<sup>28</sup> The decrease of the total IR intensity may be due to partial destruction during annealing or to a smaller transition moment of the higher frequency peak.

Support for this notion was obtained from the following observations: (1) The vibrational frequency of the ion pair peak was not influenced by the presence of a variable amount of Ar in the matrix while the vibrational frequency of the free peak showed appreciable shifts. (2) A peak 2 cm<sup>-1</sup> below that of free  $N_3^-$  was observed on four of the six isotopomers when the nitrogen deposition rate was very high (Figure 6). This peak also showed up when Ar was codeposited with  ${}^{14}N_2$ . It is assigned to free  $N_3^$ at another site. This demonstrates that the difference caused by site effects can be as small as only a few wavenumbers even for an anion. (3) The photobleaching thresholds of the two peaks differ considerably. This could only be investigated in a qualitative fashion at relatively low resolution, by using optical filters and a xenon arc lamp. In an nitrogen-argon ( $\sim$ 2:1) matrix, the maximum wavelength at which the free peak was bleached detectably was  $275 \pm 15$  nm, while for ion pair it was  $360 \pm 15$  nm. Thus, it takes about 1.1 eV less energy to remove an electron from the ion-paired  $N_3^-$  than from the free matrix-isolated  $N_3^-$ , presumably since in the ion pair, the electron transfer is to a counterion and not to the matrix conduction band.

The nature of the counterion is not known, and it is probably derived from a trace impurity species such as  $H_2O$ ,  $H_3O^+$  being a reasonable candidate. The concentration of the counterion centers probably limits the concentration of the anions that can be achieved. When an electron flood-gun was placed in front of the cold window during bombardment, no increase in the intensity of the peaks of group II was noted.

The assignment of the anionic species as  $N_3^-$  was confirmed in a definitive fashion by the observation of isotopically shifted





**Figure 6.**  $\nu_3$  vibrational frequencies of all six isotopomers of the azide anion N<sub>3</sub><sup>-</sup> obtained by the bombardment of  ${}^{14}N_2 + {}^{15}N_2$  (1:1) with 4-keV Ne and Ne<sup>+</sup> (80  $\mu$ A). Deposition rate: 10 mmol/h at 20 K. Weak peaks at 2001.0, 1990.9, 1946.9, and 1935.0 cm<sup>-1</sup> are due to  ${}^{14}N^{14}N^{14}N^{-}$ ,  ${}^{14}N^{14}N^{15}N^{-}$ ,  ${}^{14}N^{15}N^{-5}N^{-}$ , and  ${}^{15}N^{15}N^{-}$  at a different site.

peaks (Figure 6). Table II lists the experimental, calculated,<sup>27</sup> and computed vibrational frequencies  $v_3$  of the six isotopomers corresponding to free N<sub>3</sub><sup>-</sup>. For ion-paired N<sub>3</sub><sup>-</sup>, the vibrational frequency for <sup>15</sup>N<sub>3</sub><sup>-</sup> is 2009.6 cm<sup>-1</sup> (Figures 3 and 4; to be compared with 2007.3 cm<sup>-1</sup> from calculation with Herzberg's formulas<sup>27</sup>), but the intensities of the other corresponding isotopically shifted peaks in the experiments with <sup>14</sup>N<sup>15</sup>N and with mixtures of <sup>14</sup>N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> were too low to allow reliable detection.

The isotopic shifts leave no doubt that this species is a triatomic molecule with  $D_{\infty h}$  symmetry. Since it is distinct from the N<sub>3</sub><sup>+</sup> cation, whose vibrational frequencies are<sup>9.29</sup>  $v_1 = 1170$  and  $v_1 + v_3 = 2565$  cm<sup>-1</sup>, the only reasonable possibility is the N<sub>3</sub><sup>-</sup> anion. The other IR peaks of N<sub>3</sub><sup>-</sup> expected on the basis of solid-state studies are much weaker than the antisymmetric stretch and should not be observable under our conditions, given the relatively weak intensity of the 2003.5- and 2077.8-cm<sup>-1</sup> peaks.

SCF Computations on  $N_3^-$ ,  $N_{3^*}$ , and  $N_3^+$ . The computed equilibrium geometries and vibrational frequencies as well as total energies of the  $N_3^-$  singlet,  $N_3^+$  doublet, and  $N_3^+$  triplet ground states are listed in Table III. In all three cases, the symmetry of the molecule was found to be  $D_{\infty h}$ , in agreement with experimental evidence.<sup>5,20</sup> This differs from the results of previous computations,<sup>30</sup> which predicted a  $C_{\infty h}$  equilibrium geometry for the ground states of  $N_{3^*}$  and  $N_{3^+}$ , with higher total energies.

Computations were also performed on a system in which a unit positive charge was placed at the molecular axis 2 Å from the terminal nitrogen atom of  $N_3^-$  to simulate an ion pair. The calculated antisymmetric stretching frequency  $\nu_3$  was 2352.9 cm<sup>-1</sup>, a 38.3-cm<sup>-1</sup> increase relative to the 2314.6-cm<sup>-1</sup> value computed for  $\nu_3$  of free  $N_3^-$ . The computed direction of the shift supports

<sup>(29)</sup> Jacox, M. E. J. Phys. Chem. Ref. Data 1984, 13, 967.

<sup>(30)</sup> Archibald, T. W.; Sabin, J. R. J. Chem. Phys. 1971, 55, 1821.

TABLE III: Computed<sup>a</sup> Vibrational Frequencies, Bond Lengths, and Total Energies of <sup>14</sup>N<sub>3</sub><sup>-</sup>, <sup>14</sup>N<sub>3</sub><sup>-</sup>, and <sup>14</sup>N<sub>3</sub><sup>+</sup>

		4-31G*	6-311G*	exptl
N3-	<i>v</i> <sub>1</sub>	1575.1	1539.2	1344 <sup>b</sup>
•	v2	789.32	773.92	642.4 <sup>b</sup>
	$\nu_3$	2314.6	2266.3	2036.4 <sup>b</sup>
	-			2003.5°
		$(2352.9)^d$		$(2077.8)^d$
	r	1.1537	1.1504	1.1884 <sup>e</sup>
	Ε	-163.098 00	-163.303 19	
$N_3$	$\nu_1$	1508.2	1495.2	~1287 <sup>f</sup>
-	V2	615.45 <sup>g</sup>	600.92 <sup>g</sup>	472.7 <sup>f</sup>
	$\nu_3$	1713.1	1674.9	1657.5
	r	1.1570	1.1538	1.1815 <sup>h</sup>
	Ε	-163.088 09	-163.28468	
$N_3^+$	$\nu_1$	954.72	907.77	$\sim 1170^{i}$
-	$\nu_2$	385.76	368.34	
	$\nu_3$	1260.5	1248.3	~1395'
	ř	1.1850	1.1828	
	Ε	-162.756 53	-162.95461	

<sup>a</sup>RHF for <sup>14</sup>N<sub>3</sub><sup>-</sup>, UHF for <sup>14</sup>N<sub>3</sub><sup>+</sup> and <sup>14</sup>N<sub>3</sub><sup>+</sup>. Vibrational frequencies  $\overline{\nu}$  in cm<sup>-1</sup>, bond lengths r in angstroms, and total energies E in atomic units. In all cases, the calculated ground-state equilibrium geometry is  $D_{\infty h}$ . <sup>b</sup>KN<sub>3</sub> crystal.<sup>12</sup> <sup>c</sup>Free matrix-isolated N<sub>3</sub><sup>-</sup>. See text. <sup>d</sup>Ion-paired matrix-isolated N<sub>3</sub><sup>-</sup>. See text. <sup>c</sup>Gas phase.<sup>20</sup> <sup>f</sup>Matrix-isolated N<sub>3</sub>. See text. <sup>g</sup>The average of the two zero-order Renner-Teller frequencies. No effort was made to compute the spin-orbit and Renner-Teller splitting. <sup>h</sup>Gas phase.<sup>5</sup> <sup>i</sup> From the photoelectron spectrum<sup>9,29</sup> of N<sub>3</sub>. The value of  $\nu_3$  is derived from  $\nu_1 + \nu_3$  and  $\nu_1$ .

our assignment of the species responsible for the 2077.8-cm<sup>-1</sup> peak to an ion-paired  $N_3^-$  anion.

### Discussion

The Azido Radical,  $N_3$ . 1. The previously suggested pre-dissociative nature of the  ${}^{2}\Sigma_{u}^{+}$  upper state of the 272-nm transition and its dissociation channel to  $N(^2D)$  and  $N_2(^1\Sigma_g^{+})^4$  have now been proven by the observation of emission from the <sup>2</sup>D state of the N atom upon  ${}^{2}\Sigma_{u}^{+} \leftarrow {}^{2}\Pi_{g}$  excitation of N<sub>3</sub>. It accounts in a natural fashion for the short observed fluorescence lifetime.<sup>11</sup> The 1700-cm<sup>-1</sup> vibrational component reported<sup>4</sup> for the upper state has not been found in our work. Its absence has also been noted by other workers.<sup>5</sup>

2. The vibrational frequencies of 2944.9, 1657.5, and 472.7 cm<sup>-1</sup> of N<sub>3</sub>, at the most stable site can be associated with the  $\nu_1$  $+ v_3$ ,  $v_3$ , and  $v_2$  vibrations, respectively, on the basis of comparison with the computations, the IR transition moment directions, and the isotopic shifts. The symmetric stretch  $v_1$  is inactive in IR, but a value of about 1287 cm<sup>-1</sup> can be obtained from the values obtained for  $v_1 + v_3$  and for  $v_3$ . This compares well with the recent gas-phase value of  $1320 \pm 50 \text{ cm}^{-1.11}$  The assignment of vibrational frequencies to different isotopomers was made by comparison with results of quantum chemical computations and of calculations using formulas given by Herzberg.<sup>27</sup> The experimental isotopic shifts are within 5 cm<sup>-1</sup> of those obtained by quantum chemical computations and within about 3 cm<sup>-1</sup> of those obtained from Herzberg's formulas,<sup>27</sup> except for the peak at 2890 cm<sup>-1</sup>, which is 10 cm<sup>-1</sup> above the value expected from quantum chemical computation and  $7 \text{ cm}^{-1}$  higher than that obtained from calculation with Herzberg's formulas,<sup>27</sup> presumably due to a perturbation. The overall agreement leaves no doubt of the correctness of the assignment. The previous assignment<sup>10</sup> of the ground-state antisymmetric stretching vibrational frequency  $\nu_3$  as 2150 cm<sup>-1</sup> clearly must be revised.

3. The spin-orbit coupling and Renner-Teller effects produce a  ${}^{2}\Sigma_{1/2}^{+}$ , a  ${}^{2}\Delta_{5/2}$ , a  ${}^{2}\Delta_{3/2}$ , and a  ${}^{2}\Sigma_{1/2}^{-}$  level for the ground electronic state of N<sub>3</sub>, with 1 quantum of the bending vibration  $\nu_2$ . Since under our conditions only the  ${}^{2}\Pi_{3/2}$  ground vibrational level is populated and since spin-orbit coupling is weak, only the transition to the  ${}^{2}\Delta_{3/2}$  level would be expected to be intense in the IR spectrum on qualitative grounds. This accounts for the absence of other Renner-Teller peaks in our spectra. The observed frequency of the  ${}^{2}\Delta_{3/2} \leftarrow {}^{2}\Pi_{3/2}$  transition, 472.7 cm<sup>-1</sup>, is compatible with the gas-phase value of  $\omega_{2} = 457 \pm 25$  cm<sup>-1</sup>.<sup>11</sup>

TABLE IV: Ground-State Vibrational Frequencies of Isoelectronic Species (cm<sup>-1</sup>)

	$\nu_1$	v2	v <sub>3</sub>	ref
N <sub>3</sub>	1287	472.7	1657.5	
CŌ,†	1280	623	1469	а
BO <sub>2</sub>	1070	464	1322	Ь
N <sub>3</sub> -	1344	642.2	2036.4	12
$CO_2$	1388.4	667.3	2349.4	с
BO <sub>2</sub>		588	1959	d

<sup>a</sup> (a) Johns, J. W. C. Can. J. Phys. 1964, 42, 1004. (b) Mrozowski, S. Phys. Rev. 1947, 72, 691. <sup>b</sup> Johns, J. W. C. Can. J. Phys. 1961, 39, 1738. <sup>c</sup>Dennison, D. M. Rev. Mod. Phys. 1940, 12, 175. <sup>d</sup> Hisatsune, I. C.; Suarez, N. H. Inorg. Chem. 1964, 3, 168.

4. A new IR peak at 1638 cm<sup>-1</sup> obtained after the irradiation of solid KN<sub>3</sub> with UV light at 77 K was reported some time ago.<sup>31</sup> The corresponding IR spectra obtained with K<sup>15</sup>N<sup>14</sup>N<sup>14</sup>N and K<sup>14</sup>N<sup>15</sup>N<sup>14</sup>N under similar conditions were identical and contained a strong peak at 1623 cm<sup>-1</sup> and two weak peaks at 1635 and 1611 cm<sup>-1</sup>. The proposed assignment was to cyclic  $N_3$  of  $D_{3h}$  symmetry, but this geometry is Jahn-Teller unstable in the ground state. It is not clear whether there are any relations between these observations and ours. The reported<sup>31</sup> IR frequency is very close to the vibration we find for  $\nu_3$  of matrix-isolated N<sub>3</sub>, but the isotopic shift pattern is different.

The Azide Anion,  $N_3^-$ . The experimental and the theoretical evidence suggest strongly that 2003.5- and 2077.8-cm<sup>-1</sup> IR peaks are due to free and ion-paired N<sub>3</sub><sup>-</sup>, respectively. Their photodetachment thresholds in nitrogen-argon matrix ( $\sim$ 2:1), 4.5 and 3.4 eV, respectively, can be compared with the gas-phase value<sup>21</sup> of 2.76 eV.

Comparison of  $N_3^-$ ,  $N_3^+$ , and  $N_3^+$ . The computed vibrational frequencies of  $N_3^-$  and  $N_3$  are higher than the experimental values, by about 11-23% for  $N_3^-$  and by about 1-17% for  $N_3^-$  (Table III). Such errors are common for SCF computations. The vibrational frequencies<sup>9</sup> of  $N_3^+$  have been reported as 1170 and 2565 cm<sup>-1</sup> as deduced from the photoelectron spectra of  $N_3$ . The former was assigned to  $v_1$  and the latter to either  $v_3$  or  $v_1 + v_3$ .<sup>9,29</sup> Our computations suggest strongly that the  $v_1 + v_3$  assignment of the 2565-cm<sup>-1</sup> peak is right. Note that even assuming this assignment, the computed frequencies are lower than the reported values by about 11-29%. This is an unusual sign for an error in an SCF computation, and we suspect that the accuracy of the frequencies derived from the photoelectron spectrum is low.

 $N_3$  is just one "nonbonding" electron short of  $N_3^-$ , and  $N_3^+$ is just one "nonbonding" electron short of  $N_3$ . It was believed at one time that the vibrational frequencies of N<sub>3</sub> should be essentially the same as those of N<sub>3</sub>, because of the "nonbonding" nature of the electron.<sup>32,33</sup> Our results certainly show that this is not so. Indeed, although the "nonbonding" electrons do not affect the bond lengths much, they contribute significantly to the force constants of these three species. Similar behavior has been noted for the isoelectronic species  $CO_2$  and  $BO_2^-$  compared with  $CO_2^+$  and  $BO_2$  (Table IV).

Linear extrapolation of the square of the experimental vibrational frequency  $v_3$  from  $N_3^-$  (2003.5 cm<sup>-1</sup>) to  $N_3$ · (1657.5 cm<sup>-1</sup>) and beyond to  $N_3^+$  predicts a vibrational frequency  $\nu_3$  of 1217  $cm^{-1}$  for  $N_3^+$  and supports the assignment of the 2565- $cm^{-1}$  vibration to  $v_1 + v_3$  of  $N_3^+$ .

Note Added in Proof. The  $v_3$  fundamental of N<sub>3</sub> has recently been observed in gas-phase absorption at 1644.6784 cm<sup>-1</sup>, in excellent agreement with our results: C, Brazier, P. Bernath, J. Burkholder, and C. Howard, submitted for publication. We are grateful to Prof. Bernath for sharing this information with us.

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