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# Matrix effects on radiative and radiationless rates of NBr b ${}^{1}\Sigma^{+}$ and a ${}^{1}\Delta$ trapped in solid argon

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NBr in solid argon has been excited to the  $b^{1}\Sigma^{+}$  state with a pulsed tunable dye laser. In addition to the well-known fluorescence spectrum of the *b* state, infrared emission from the vibrationally relaxed  $a^{1}\Delta$  state was detected at 1086 nm. Three major trapping sites were resolved in absorption and fluorescence excitation spectra of the *b*-*X* system. Additional sites could be identified in the excitation spectrum of the *a* state, which is populated via the *b* state by internal conversion. There is a weak site effect on the lifetime of the vibrationally relaxed *b* state, which varies between 40 and 30  $\mu$ s. Vibrational relaxation rates in the *b* state show a stronger site dependence. Internal conversion from  $b^{1}\Sigma^{+}$  to  $a^{1}\Delta$  accounts for <0.1% to at least 17% of the decay rate of NBr  $b^{1}\Sigma^{+}$ , v = 0. Orbitally forbidden transitions to the  $X_{1}0^{+}$ component of the ground state were identified 23.0 to 25.5 cm<sup>-1</sup> on the high-energy side of the more intense  $a^{1}\Delta \rightarrow X_{2}1^{\pm}$  transition of several sites. The lifetime of the *a* state varies between  $152 \pm 12$  ms in the least perturbed site and  $121 \pm 15$  ms in the site with the strongest  $a^{1}\Delta \rightarrow X_{1}0^{+}$  forbidden component. NBr trapped in double vacancies of pure fcc argon, of single stacking faults, and of multiple stacking faults (hcp pockets) in argon, can account for the sites.

## I. INTRODUCTION

The nitrogen monohalides NX (X = I, Br, Cl, F) have a  $X^{3}\Sigma^{-}$  ground state and two electronically excited states of fairly low energy,  $a^{1}\Delta$  and  $b^{1}\Sigma^{+}$ . Transitions between these states are strongly forbidden by electric dipole selection rules. Increasing spin-orbit and spin-spin coupling enhances the transition probabilities in the heavier monohalides, which are best described in the  $\Omega$  notation of Hund's coupling case c.<sup>1</sup> In this notation the  $X^{3}\Sigma$  ground state splits into  $\Omega = 0$  and  $\Omega = \pm 1$  components of slightly different energies, and the transitions  $b 0^+ \leftrightarrow X_1 0^+, X_2 1^{\pm}$  as well as  $a2^{\pm} \rightarrow X_2 1^{\pm}$  become electric dipole allowed, whereas the transition  $a2^{\pm} \rightarrow X_10^+$  remains forbidden in the gas phase by the  $\Delta \Omega = 0, \pm 1$  selection rule. There is, however, theoretical and experimental evidence that gas phase selection rules may be relaxed by gas-solvent interactions in condensed media.<sup>2-9</sup> For example Minaev<sup>4</sup> has calculated that the transition probability of the strongly forbidden  $a^{1}\Delta_{g} - X^{3}\Sigma_{g}^{-}$  infrared atmospheric band of molecular oxygen increases in collisions with various molecules by 2-3 orders of magnitude. Similar effects must be envisaged for electronically excited species in low-temperature matrices, and have indeed been reported.<sup>5-9</sup> Very little is known about the effect of trapping site geometry in rare gas host crystals on symmetry-forbidden electronic transitions, although heterogeneous structure in electronic spectra of matrix-isolated species is often assigned to multiple trapping sites.<sup>10</sup> However, the identity of the trapping sites is not often known. A site effect on the rate of nuclear spin relaxation of CH4 in various rare gas solids has been observed by Jones et al.<sup>11</sup>

We have recently reported on laser-induced fluorescence spectra, lifetimes, and relaxation dynamics of matrixisolated NI  $X^{3}\Sigma^{-}$ ,  $b^{1}\Sigma^{+}$ , and  $a^{1}\Delta^{.12}$  Preliminary evidence

was presented that the  $\Delta \Omega = 0, \pm 1$  selection rule was indeed violated in the a-X spectrum of NI. However, the spectrum was unavoidably broadened by doping with N2, and could not be analyzed in detail. Here we present an extension of this study to the next lighter nitrogen monohalide NBr in pure argon matrices. The gas phase spectroscopic constants of the X and b states of this species are known from highresolution work of Milton *et al.*,<sup>1</sup> while matrix data are available from IR absorption work,<sup>13</sup> and from a laser-induced fluorescence study of NBr  $b^{1}\Sigma^{+}$  in argon by Miller and And rews.<sup>14</sup> These authors report lifetimes of  $40 + 4 \mu s$  and ~25  $\mu$ s for v' = 0 and 1. Near IR emission of NBr  $a^{-1}\Delta$  has not been previously observed in matrices, but was discovered in the gas phase by Pritt et al.<sup>15</sup> In a recent attempt to determine the radiative lifetime of the b and a states by Stern-Volmer extrapolation of decay rates in the gas phase to zero pressure, values of 40 and 800  $\mu$ s were obtained.<sup>16,17</sup> While the former value agrees well with the matrix result, a lifetime of 800  $\mu$ s seems unreasonably short for such a strongly forbidden transition. In fact, a lifetime of only 2.1 ms has been inferred for the  $a^{1}\Delta$  state of NCl on the basis of the same experimental technique,<sup>16</sup> inconsistent with recent theoretical predictions of 1.1 s<sup>18</sup> and 1.9-2.9 s<sup>19</sup> which are, however, in reasonable agreement with our preliminary matrix value of 1.46 s.12

While the *b* state of NBr can be readily accessed from the ground state by absorption of laser radiation,<sup>14</sup> subsequent population of the a <sup>1</sup> $\Delta$  state by matrix-induced internal conversion occurs with low efficiency in pure argon, giving rise to a poor signal-to-noise ratio of the  $a \rightarrow X$  emission near 1086 nm. This is why we could only give a rough estimate of 500 ms for the *a* state lifetime of NBr in solid argon in a recent publication.<sup>12</sup> Subsequent improvements in our matrix preparation technique rendered possible a more detailed study, the results of which are presented in this paper.

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## **II. EXPERIMENT**

The matrices were deposited at 5, 13, or 25 K on a gold plated copper disk in a pumped helium transfer cryostat which has been described elsewhere.<sup>12</sup> The gases  $Ar/N_2/Br_2$  (final pressure 800 Torr) were premixed in a Pyrex bulb in ratios of 4000:1:1 and 20 000:1:1 in a high-vacuum gas handling system, passed through a microwave discharge, and sprayed on the cold surface through a Pyrex orifice of 0.5 mm diameter. The discharge pressure was stabilized at 3 Torr for optimum NBr yields.

After deposition the matrix was annealed at 30 K for 15 to 30 min. Three vibronic levels of NBr  $b^{1}\Sigma^{+}$  were excited with a nitrogen laser pumped tunable dye laser (Lambda Physik M 1000/FL 2000) at a pulse repetition rate of 118 Hz, using DCM laser dye for the v' = 0 and 1 levels, and Sulfrhodamin B for v' = 2. The fluorescence was focused on a Spex 1400 monochromator. The spectral range from the visible up to 1700 nm was covered with two photomultipliers and a Ge detector, as previously described.<sup>12,20</sup> Lifetimes were measured with a Le Croy 9400 125 MHz digital storage oscilloscope preceded by a PAR 115 wideband amplifier. The WP01 waveform processing option of the scope was used for signal averaging. The module was triggered by the laser to measure *b*-state lifetimes in the  $\mu$ s time range. To measure the much longer lifetime of the a-state, a slow mechanical chopper was installed in the laser beam, which triggered the Le Croy at its chopping rate of 1-2 Hz. Typically  $10^4$  scans were averaged for *b*-state lifetimes, and  $10^3$  for the a-state.

To measure the b-X transition of NBr in absorption, matrices were deposited on a sapphire window and placed in the optical path between the exit slit of the monochromator and the Varian VPM 159A photomultiplier. Light from a tungsten filament lamp was focused on the entrance slit. Spectra of a pure argon matrix, and of matrices containing NBr radicals, were digitally stored and divided by computer to correct for light attenuation by scattering.

#### **III. RESULTS**

#### A. Spectral observations

Our fluorescence and excitation spectra of NBr  $b^{1}\Sigma^{+}$ , v' in solid argon agree within experimental accuracy with the

TABLE I. NBr in different trapping sites of an argon matrix deposited at 5 K, Br<sub>2</sub>:N<sub>2</sub>:Ar = 1:1:20 000. Line positions *E* and their differences  $\Delta E$  relative to site 1 are given in cm<sup>-1</sup>. Intensities of sites 1 to 5 refer to peak areas in excitation spectra of the broadband-detected (0,3) band in  $b \rightarrow X_1$ , and of the (0,0) band in  $a \rightarrow X_2$ . They are corrected for variations in dye laser output and spectral transmission of the detection system, and normalized to the intensity of site 1 in each electronic transition.

	$b^{1}\Sigma^{+}\leftrightarrow X^{3}\Sigma^{-}$		$a^{1}\Delta \rightarrow x_{2}^{2}\Sigma^{-}$			
Site	E (excitation, 0,0 band)	$\Delta E$	Intensity (excitation sp.)	E (emission, 0,0 band)	$\Delta E$	Intensity (excitation sp.)
1	14 702.4	0	1.000	9211.3	0	1.00
2	14 694.6	8.2	0.580	9205.6	5.7	1.04
2'	14 691.5	11.0	0.000 <sup>a</sup>	n.d.	n.d.	1.24
3	14 673.7	28.7	0.024	9194.1	17.2	1.70
4	14 667.7	34.7	0.010	9189.5	21.8	2.63
5	14 613.9	88.5	0.980	9136.9	74.4	4.18

\* Only observed in excitation spectrum of broadband-detected  $a \rightarrow X$  emission.

spectroscopic constants of the  $b^{1}\Sigma^{+}$  and  $X^{3}\Sigma^{-}$  states published by Miller and Andrews.<sup>14</sup> The  $T_e$  value reported by these authors coincides with the second highest site of NBr identified in this work (site 2 in Table I). Emission spetra were obtained by exciting the vibronic levels v = 0, 1, 2 of NBr  $b^{1}\Sigma^{+}$  with the tunable dye laser. In addition to the b-Xbands reported by Miller and Andrews, which involve mainly the lower component  $X_10^+$  of the electronic ground state,<sup>15</sup> a novel band was observed at 1086 nm, which we assign to the (0,0) band of NBr  $a2^+ \rightarrow X_2 1^{\pm}$ . This assignment is based on the following evidence: (a) the wavelength, which is only slightly red shifted with respect to the (0,0)band in the gas phase at 1078 nm<sup>15</sup>; (b) the excitation spectrum, which coincides with the excitation and absorption spectrum of the precursor state  $b^{1}\Sigma^{+}$ , (c) the very long lifetime of the emitter.

Both heterogeneous and homogeneous fine structure could be resolved in the (v',v'') bands of the  $b \leftrightarrow X$  and  $a \rightarrow X$ spectra in argon: (a) heterogeneous structure, which we attribute to well-defined subsets of NBr radicals in different trapping sites; after annealing of the matrix these subsets became well separated, could be individually excited with the laser, and their fluorescence could be observed independently; (b) the zero-phonon lines (zpl's) of two sites were accompanied by local phonon progressions both in excitation and emission, showing the same temperature dependence as previously observed in the b-X bands of matrixisolated NI<sup>12</sup>; (c) in addition to local phonon progressions, several sites in the  $a \rightarrow X$  transition exhibit a temperatureindependent high energy satellite, arising from the orbitally forbidden transition to the lower  $X_10^+$  component of the electronic ground state.

#### 1. Site structure in the b ${}^{1}\Sigma^{+}-X {}^{3}\Sigma^{-}$ spectra

An absorption spectrum of NBr in an annealed matrix in the region of the (0,0) band of b-X is shown in Fig. 1. Although the absorption is weak, owing to the poor absorption cross section of the partially forbidden transition, three absorption lines are clearly resolved on a structured background. The same features, plus some weaker lines, are also observed in the broad-band detected excitation spectra of the b-X emission after annealing, Figs. 2(a)-2(c), which illus-



FIG. 1. (0,0) band of NBr  $b^{1}\Sigma^{+}-X^{3}\Sigma^{-}$  in absorption. The matrix (N<sub>2</sub>:Br<sub>2</sub>:Ar = 1:1:4000) was deposited at 13 K, then 20 min annealed at 30 K. Absorption was measured at 8 K.

trates the effect of matrix composition and deposition temperature on the linewidth. This and other excitation spectra were obtained by scanning the laser across the (0,0) band, while detecting the (0,3) band in emission with a small monochromator of 25 cm focal length. At 2 mm width the slit function (12 nm FWHM) was sufficiently wide to transmit the (0,3) bands of all sites simultaneously. The excitation spectra were corrected by computer for variation of laser power, spectral transmission and slit function of the monochromator, and detector sensitivity.

Five narrow lines in the excitation spectrum of the b state have been assigned to NBr radicals in different trapping sites of the argon matrix. They could be individually excited

by tuning the laser to each of the marked lines in Figs. 2(a)– 2(c). The corresponding site-resolved (0,1) bands in the *b*-*X* emission spectrum, recorded at 0.04 nm spectral resolution, are shown in Fig. 3. They differ in energy and fine structure. The sites were numbered in order of decreasing energy in emission and absorption. Table I lists wave numbers of the zpl in each (0,0) band in absorption and emission, as well as the shifts  $\Delta E$  relative to the zpl of the highest energy component, site 1. The spacing  $\Delta E_{(1-5)}$ between the zpl's 1 and 5 in other bands of the *b*-*X* spectrum decreased slightly with increasing v', e.g., from  $\Delta E_{(1-5)}$ = 88.5 cm<sup>-1</sup> in the (0,0) band to 78.6 cm<sup>-1</sup> in the (1,0) band.

Each site emits a prominent zpl, and a weak structured (sites 1 and 2), or structureless sideband (sites 3 and 4). The sideband intensity of site 5 is comparable to sites 1 and 2, but the structure is different, with a weak line  $9 \text{ cm}^{-1}$  red shifted with respect to the zpl. The line width (FWHM) at 5 K is 3–3.5 cm<sup>-1</sup>, similar to the line width in the excitation spectrum at the same temperature and concentration (sites 1, 2, and 5), and 4.5 cm<sup>-1</sup> (sites 3 and 4). The widths of sites 1–4 increase slowly with temperature to about 6.5 cm<sup>-1</sup> at 25 K, while the width of site 5 doubles in the range 5–10 K.

In order to determine the thermodynamically most stable site of NBr in argon, we have sandwiched a standard matrix of NBr in argon ( $N_2:Br_2:Ar = 1:1:4000$ ) with a protective layer of pure xenon. This way it was possible to anneal the matrix at 45 K with insignificant evaporation losses. In the *b*-X fluorescence excitation spectrum of the annealed matrix all the lines attributed to sites 1-4 had disappeared,



FIG. 2. Excitation spectra of NBr in the  $b^{1}\Sigma^{+}$  and  $a^{1}\Delta$  states, as function of matrix composition (N<sub>2</sub>:Br<sub>2</sub>:Ar) and deposition temperature (DT): (a) b state, 1:1:20 000, DT 5 K; (b) b state, 1:1:4000, DT 13 K; (c) b state, 1:1:20 000, DT 25 K; (d) a state, 1:1:20 000, DT 5 K; (e) a state, 1:1:4000, DT 13 K; (f) 1:1:20 000, DT 25 K. All spectra recorded at 8 K.



FIG. 3. (0,1) bands in the b-X fluorescence of selectively excited NBr radicals in sites 1 to 5. Matrix mixing ratio  $N_2$ :Br<sub>2</sub>:Ar = 1:1:4000. Spectra recorded at 8 K.

while site 5 at 14 614 cm  $^{-1}$  (FWHM 3 cm $^{-1}$  at 5 K) was still present.

## 2. Site structure in the a2±-X<sub>2</sub>1± spectrum

Excitation spectra of the long-living infrared emitter at 1086 nm are reproduced in Figs. 2(d)-2(f). Excepting the line at 14 691.4 cm<sup>-1</sup> of an additional site 2', which was not detected in the fluorescence excitation spectrum of the *b* state owing to very efficient internal conversion, the wave numbers of the lines in Figs. 2(d)-2(f) and 2(a)-2(c) are in excellent agreement. The relative intensities of the lines, however, are different in both sets of excitation spectra. It is concluded that the metastable state emitting at 1086 nm is NBr  $a2^{\pm} \equiv a^{-1}\Delta$ .

Although internal conversion of NBr  $b^{1}\Sigma^{+}$  to  $a^{1}\Delta$  is sufficiently effective in solid argon to study the spectrum of the successor state with 0.1 nm spectral resolution, the emission is much less intense than the emission of the *b* state. Only emission from the vibrationally relaxed *a* state could be detected. Figure 4 presents *a*-state spectra emitted by five subsets of NBr radicals in different trapping sites. The labeling of the zpl's corresponds to the numbering of the sites in Figs. 2 and 3. Clearly no site scrambling occurs in the internal conversion process. However, taking again site 1 as a reference, the shifts  $\Delta E$  of the zpl's have definitely decreased by 15%-40% in the *a*-X transition; wave numbers of the zpl's and shifts  $\Delta E$  in this band are listed in columns 5-7 of



FIG. 4. (0,0) bands in the a-X fluorescence of selectively excited NBr radicals in sites 1 to 5. Matrix mixing ratio N<sub>2</sub>:Br<sub>2</sub>:Ar = 1:1:4000. Asterisks denote forbidden  $a2^{\pm}-X_10^+$  components of the bands. Spectra recorded at 8 K.

Table I. Furthermore, the low-energy phonon wing of the bands is weaker than in the corresponding b-X bands (site 2), or has completely disappeared (sites 1, 3, and 4), while new lines appear on the high energy side of the zpl's. The intensity of the first high-energy satellite of each zpl increases with temperature. The asterisks in Fig. 4 denote other satellite lines which are shifted 23-25.5 cm<sup>-1</sup> to higher energy. The intensity ratios of these satellite lines and the corresponding zpl's are temperature independent, and do not vary from matrix to matrix. The excitation spectra of the zpl and of the high energy satellite are identical, showing that both are due to the same emitter. The temperature dependence of the zpl's and their high-energy satellites in the a-X spectra of sites 1 and 2 are shown in Fig. 5.

#### 3. Effects of impurities

Milligan and Jacox in their pioneering work on the IR absorption spectrum of NBr in solid argon assigned two lines at 680 and 691 cm<sup>-1</sup> to fundamentals of the radical in different trapping sites.<sup>13</sup> Heterogeneous structure was also observed by Miller and Andrews in the laser-induced fluorescence spectrum of NBr  $b^{1}\Sigma^{+}$  in solid argon.<sup>14</sup> However, these authors attributed the multiline structure of the bands to the presence of impurities, because some lines could be enhanced by doping the argon matrix with oxygen. Their matrices were prepared at much higher guest-host ratios,



FIG. 5. a - X spectra of NBr in trapping sites 1 and 2 in the temperature range 5–20 K. The peaks  $a_1$  and  $a_2$  are zpl's of transitions to the  $X_2 1^{\pm}$  and  $X_2 0^{+}$  components of the ground state.

 $N_2:Br_2:Ar = 1:2:400$  for the fluorescence study, and up to 1:1:100 for the absorption measurements, and could not be annealed without destruction of NBr. This contrasts with our observation that annealing at 30 K was necessary to obtain sharp excitation, absorption, and fluorescence spectra. Figure 2 shows that changing the  $N_2:Br_2:Ar$  ratio from 1:1:20 000 to 1:1:4000 in our system had no significant effect on the relative line intensities, while increasing the linewidths in the excitatation spectra from 3 to 5–6 cm<sup>-1</sup>.

The detrimental effect of annealing on NBr in the matrices prepared by Miller and Andrews is probably due to the higher guest-host ratios used by these authors, as well as to different kinetics of NBr formation: The matrices of Miller and Andrews were photolyzed during deposition with a separate windowless argon resonance lamp, thereby generating atoms inside the solid host. A significant fraction of the atoms does not react at the low temperature. Annealing the matrix mobilizes unreacted atoms, particularly nitrogen atoms, which give rise to chemiluminescence and NBr destruction. In our system atoms were generated in the gas phase by a microwave discharge. The discharge products were sprayed on the cold surface through a pinhole. Under these conditions atom recombination on the surface of the matrix is very efficient, and only a small amount of unreacted nitrogen atoms is mobilized upon subsequent annealing.

The argon used for matrix preparation in this work had



FIG. 6. Effect of impurities on excitation spectrum of NBr  $a^{1}\Delta$ . All matrices deposited at 5 K, annealed for 30 min at 30 K, and excited at 8 K: (a) N<sub>2</sub>:Br<sub>2</sub>:Ar = 1:1:20 000; (b) 5:1:20 000; (c) 1:1:20 000 + 12.5 ppm O<sub>2</sub>; (d) 1:1:20 000 + 100 ppm O<sub>2</sub>.

a stated impurity level of 5 ppm  $N_2$  and 3 ppm  $O_2$ . The effect of impurities on the sites was tested in doping experiments, i.e., by increasing the  $N_2$  mixing ratio from 50 ppm in the standard 1:1:20 000 matrix to 200 ppm in the doped matrix, or by adding between 12.5 and 100 ppm oxygen. The most obvious effect on the excitation spectrum of the b state was line broadening, similar to the effect of increasing the guesthost ratio from 1:1:20 000 to 1:1:4000 in Figs 2(a) and 2(b), and a selective intensity reduction of the site 2 line, which was particularly notable in the presence of O2. The effect of impurities on the excitation spectrum of the a state (excitation via  $b^{1}\Sigma^{+}$ ) was stronger, as evidenced in Fig. 6: apart from line broadening, changes in relative intensities occurred. In particular, emission from sites 3 and 4 was significantly reduced. We attribute these effects to impurity-induced crystal imperfections, rather than to nearest neighbor interactions with NBr. The statistical probability of finding an impurity molecule (N<sub>2</sub>, Br<sub>2</sub>, or oxygen) next to NBr is very low, much less than 1%, at the guest-host ratios and impurity levels prevalent in this work.<sup>21,22</sup> We have previously observed the effect of nitrogen as nearest neighbor on the *b*-state excitation spectrum of NI. Pairs of NI  $\cdot$  N<sub>2</sub> were prepared by photolyzing IN<sub>3</sub> in solid argon (guest-host ratio of 1:1000). The excitation spectrum was a broad feature of 140 cm<sup>-1</sup> FWHM, comparable with the excitation spectrum of NI in a mixed matrix of 10% N<sub>2</sub> in argon, but quite different from the narrow excitation spectrum of isolated NI in pure argon.<sup>12</sup> Attempts to prepare NBr  $\cdot$  N<sub>2</sub> by in situ photolysis of BrN<sub>3</sub> were defeated by the explosive nature of the azide.

We conclude that the heterogeneous structure in our NBr spectra must be assigned to trapping sites in a pure argon host.

#### **B. Lifetime measurements**

The lifetime measurements reported in this paper were selective with respect to both excitation and detection wavelength. This ensured that only one site in a specific vibronic level was analyzed at a time. The decay of the vibrationally relaxed b and a states was strictly monoexponential, and lifetime uncertainties on the 1% level could be achieved in single measurements. Lifetimes were measured 3 to 4 times at each temperature, and somewhat larger uncertainties resulted from the scatter between these results. In measurements of the much faster decay of NBr  $b^{1}\Sigma^{+}$ , v' = 2 a slow underlying component with the lifetime of the relaxed b state could not be completely eliminated. Lifetime measurements of the v' = 1 level were practically unaffected by this background component.

#### 1. Lifetimes of NBr b ${}^{1}\Sigma^{+}$

Site-resolved lifetimes of the vibrationally relaxed b state were measured in the range 5-30 K, and were found to be temperature independent within experimental scatter. Averages of the lifetimes are listed in the second column of Table II. The lifetimes in sites 1 and 2 are identical within experimental accuracy, and in excellent agreement with the reported value of  $40 \pm 4\mu s$  in argon.<sup>14</sup> The lifetimes in sites 3 and 4 are significantly shorter by ~20%, while site 5 takes

TABLE II. Site-resolved lifetimes of NBr  $b^{1}\Sigma^{+}$ , v' = 0, 1, 2, and  $a^{1}\Delta v' = 0$ , in an argon matrix, Br<sub>2</sub>:N<sub>2</sub>:Ar = 1:1:4000. The data are averages over the temperature range 5-30 K, unless otherwise noted.

<b>C</b> '.	Lifetir			
No.	v'=0	v'=1	<i>v</i> ′ = 2	in ms, $v' = 0$
1	39.8 ± 1.3	$1.67 \pm 0.06$	0.77 ± 0.01	$152 \pm 12$
2	38.7 ± 0.9	$1.62 \pm 0.15$	0.76 ± 0.09	$121 \pm 15$
3	$31.5 \pm 1.1$	n.d.	n.d.	149 ± 12
4	30.2 ± 1.6	n.d.	n.d.	$133 \pm 11$
5	$34.9 \pm 1.3$	$\sim 10^{a}$	n.d.	$144 \pm 14$

\*Extrapolation to 0 K, cf. Fig. 8.

an intermediate position.

Figure 7 summarizes the site-resolved lifetimes of NBr  $b^{1}\Sigma^{+}$ , v' = 1 and 2 (sites 3 and 4 could not be studied because of intensity problems). The vibronic lifetimes in sites 1 and 2 are temperature independent and practically identical, and much shorter than the temperature dependent lifetime of v' = 1 in site 5, which is, however, still significantly shorter than the reported estimate of 25  $\mu$ s for this vibronic level.<sup>14</sup> Table II lists average vibronic lifetimes of NBr  $b^{1}\Sigma^{+}$ , v' for the temperature-independent sites 1–4, while the lifetime of 10  $\mu$ s in site 5, v' = 1 was obtained by extrapolation to 0 K.

## 2. Lifetimes of NBr a 14

The site-resolved lifetimes of the  $a^{1}\Delta$  state were temperature independent in the range 5-30 K. The lifetimes in the last column of Table II are averages of several determinations at different temperatures. There are slight but significant differences between the lifetimes of sites 1, 3, and 5 on the one hand, and sites 2 and 4 on the other. Separate measurements on the zpl of site 2, and on its satellite line which is labeled with an asterisk in Fig. 4, yielded identical lifetimes.



FIG. 7. Site-selective lifetimes of NBr  $b^{1}\Sigma^{+}$ , v' = 1 and 2 in the temperature range 5-30 K. ( $\Diamond$ ) v' = 1 site 1; (O) v' = 1 site 2; ( $\mathbf{\nabla}$ ) v' = 1 site 5; ( $\times$ ) v' = 2 site 1; ( $\Box$ ) v' = 2 site 2. Note change of scale for lifetimes of site 5.

## IV. DISCUSSION

## A. Trapping sites

The small difference in the reduced masses of  ${}^{14}N^{79}Br$ and  ${}^{14}N^{81}Br$ , which are about equally abundant, gives rise to isotope splittings in the *b-X* bands of NBr, as previously noted by Miller and Andrews.<sup>14</sup> We have been able to partially resolve an isotope splitting of 1.2 cm<sup>-1</sup> (0.06 nm) in the (0,1) band of site 1. Under the conditions of this study, however, the isotope splitting was always negligible compared with the site splitting to be discussed in the following sections.

The "size" of NBr can be estimated from a two-center Lennard-Jones model,<sup>23</sup> which has been previously adopted by Abbate and Moore to estimate the size of HCN in solid argon.<sup>24</sup> Using  $\sigma = 0.3314$  nm for the LJ diameter of the nitrogen atom,  $\sigma = 0.3538$  nm for Br,<sup>23</sup> and 0.1787 nm for the bond length in NBr<sup>25</sup> yields an egg-shaped radical 0.521 nm long and 0.354 nm in diameter (0.56 nm long and 0.397 nm in diameter, if  $d_0 = 2^{1/6} \times \sigma$  at the potential minimum is preferred for the atomic diameter). Comparing this with the nearest-neighbor distance of 0.3755 nm in solid argon<sup>26</sup> shows clearly that the radical must be trapped in a two-atom substitutional site.

How can our observation of five energetically distinct trapping sites [six sites, if site 2' in Fig. 6(a) of the a-state excitation spectrum is included] of NBr in pure argon be reconciled with the conclusion that the radicals reside in two-atom substitutional sites? The thermodynamically stable fcc phase of solid argon provides only one such site with  $D_{2h}$  symmetry, but additional sites can arise in a metastable hcp environment. Although fairly high mixing ratios of N<sub>2</sub> in argon are required to stabilize the hcp phase at low temperature,<sup>27</sup> metastable structures may result when an effusive beam of argon is deposited on a cold surface. The persistence of metastable sites in argon has recently been demonstrated in a FTIR study of CH4: the radical was detected in one-atom subtitutional sites of  $O_h$  and  $C_{3\nu}$  symmetry in about equal proportions.<sup>11</sup> The pulse-deposited matrices (mixing ratios between 1:500 and 1:10 000) had been annealed at 30 K.

An argon crystal can be visualized as layers of closest packed spheres stacked in the order ABCABC ..., giving rise to uniform two-atom substitutional sites of  $D_{2h}$  symmetry. When NBr is adsorbed parallel or (less likely) perpendicular to a surface A, a local stacking fault of the type ABCABACB... may be induced. When NBr is oriented parallel to surface A, the two-atom substitutional site has  $C_{2\nu}$ symmetry, whereas radicals oriented perpendicular to the surface replace two argon atoms from adjacent layers BA. The resulting cage of  $C_s$  symmetry provides two trapping sites, because NBr can be oriented either parallel or antiparallel to BA. The latter orientation is more likely, since adsorption of the radical by the more polarizable Br end should be energetically favored. Double (or multiple) stacking faults (hcp pockets) of the type ABCABABC ... or ABCA-**BABAB...** furnish double vacancies of  $C_{2h}$  symmetry when two atoms are removed from adjacent layers BA. Two atoms removed from layer  $\overline{B}$  leave a cage of  $C_{2v}$  symmetry, which differs, however, from the  $C_{2\nu}$  cage in layer **<u>B</u>** of a single stacking fault when the next-nearest layers of the host crystal are taken into account. This difference is likely to become energetically significant when the crystal is allowed to relax around the trapped species.

In summary, NBr can be trapped in six unequal sites in solid argon, in agreement with the heterogeneous splittings resolved in the b-X and a-X spectra of the radical. There should be only one persistent two-atom substitutional site, site 5 according the 45 K annealing experiment, which has  $D_{2h}$  symmetry in the thermodynamically stable fcc lattice, and which corresponds with the strongest feature in the absorption spectrum, Fig. 1. This and other tentative assignments are listed in Table III. Because double or multiple stacking faults are less likely to occur<sup>27</sup> than single stacking faults of the type ABCABACBAC ..., we have assigned the second strongest features 1 and 2 in the b-X spectra to the more abundant  $C_{2v}$  and  $C_s$  sites of such single stacking faults. Further arguments in support of the assignments in Table III will be given in the following sections.

#### **B. Band structures**

#### 1. Phonon structure in the b-X bands

The structure of the b-X bands in Fig. 3 varies as function of trapping site: the bands of sites 1 and 2 exhibit similar structures on the low- and high-energy sides of a strong zpl. The zpl's of sites 3-5 adjoin with normal phonon side bands. Superimposed on the phonon side band of site 5 is a very weak low energy  $(-9 \text{ cm}^{-1})$  satellite. The structure of the site 1 and 2 bands, which resembles the (better developed) line structure in the b-X bands of matrix-isolated NI,<sup>12</sup> is assigned to a local resonant mode (librational or translational), which can be simultaneously excited or deexcited in vibronic transitions of the guest. Low-energy satellites of the zpl arise from changes  $\Delta n = n' - n'' \leq -1$  of the resonant mode quantum number in the electronic transition. High energy satellites (hot bands,  $\Delta n \ge +1$ ) evolve at elevated temperatures when quantum states  $n' \ge 1$  are populated.

Figure 8 (right-hand panel) shows that the temperature dependence of the emission (0,1 band of site 1) fits this model: the low-energy satellite c of the zpl a is temperature independent (the temperature dependent continuous back-

TABLE III. Assignment of zpl's in the b-X and a-X spectra of NBr to twoatom substitutional sites in argon.

zpl No.	Type of trapping site	Symmetry of trapping site	Remarks
1	Single stacking fault	C <sub>2v</sub>	
2	Single stacking fault	$C_s$	Differ by opposite
2'	Single stacking fault	$C_s$	orientation of NBr
3	Multiple stacking faults	$C_{2v}^{a}$	
4	Multiple stacking faults	$C_{2h}$	
5	fcc	$D_{2h}$	Thermodynamically most stable site

\* Differs from site 1 when next-nearest neighbors and relaxation of the matrix are taken into account.



FIG. 8. Temperature dependence of NBr b-X spectra in site 1. Left: fluorescence excitation spectrum of (0,0) band, detected at 14 032 cm<sup>-1</sup> (0,1 band). Right-hand side: Corresponding (0,1) band in emission, laser locked on zpl of (0,0) band. Spectral resolution reduced from 0.04 nm at 5 K to 0.16 nm at 25 K.

ground must be subtracted), and a high-energy satellite **b** develops. The corresponding excitation spectrum is shown on the left panel of Fig. 8. It behaves approximately like the mirror image of the emission spectrum, as predicted by the model. However, while the resonant mode of NI in argon has the same frequency of 15 cm<sup>-1</sup> in the ground and electronically excited state,<sup>12</sup> the spectrum of NBr is consistent with different resonant mode frequencies of 18.9 cm<sup>-1</sup> in the ground state, and 16.4  $cm^{-1}$  in the excited state. Note that the peak maximum of the high-energy satellite c in the excitation spectrum (b in the emission spectrum) undergoes a temperature-dependent shift to lower energies. This is caused by line broadening, and in consequence coexcitation of the low energy site 2, which superimposes in emission on the spectrum of site 1.

#### 2. Structure of the a-X bands

The five a-X bands in Fig. 4 correspond with five selectively excitable sites of NBr in the  $b^{1}\Sigma^{+}$  precursor state. The identity of the sites is obviously retained in the radiationless transition to the *a* state. The structure of the a-X bands in Fig. 4 differs systematically from the b-X bands in Fig. 3: While phonon side bands or satellites are absent or weak on the low-energy side of the zpl's, up to four blue-shifted satellites can be identified. The blue shift of the first high-energy satellite varies in the order 12.8, 11.2, 8.5, 6.7, and 9.5 cm<sup>-1</sup>

in sites 1–5. A particularly intense high-energy satellite in site 2 is marked with an asterisk in Fig. 4: the blue shift of this line amounts to  $23 \text{ cm}^{-1}$ . This value agrees approximately with the shifts of some less prominent satellites in other sites, which are also marked with asterisks in Fig. 4 (blue shifts in brackets): site 4 (24.5 cm<sup>-1</sup>), site 5 (25.5 cm<sup>-1</sup>), and site 1 (23 cm<sup>-1</sup>, very weak).

The temperature dependence of the high-energy satellites of sites 1 and 2 is shown in Fig. 5. The intensity of the first high-energy satellite  $b_1$  increases with temperature, as expected for a hot band arising from a resonant mode of very low frequency in the a state (frequencies between 6.7 and 12.8 cm<sup>-1</sup>, see above). The prominent high-energy satellite in site 2 ( $a_2$  in Fig. 5), however, is not sensitive to temperature variations, and thus cannot be assigned to local modes in the a state. We conclude that this line represents the orbitally forbidden transition  $a2^{\pm} \rightarrow X_10^+$ , while the zpl  $a_1$  is assigned to the regular transition  $a2^{\pm} \rightarrow X_2 1^{\pm}$ . The upper and lower bounds of the spin-spin coupling constant  $\lambda$  and other spectroscopic constants of NBr  $X^{3}\Sigma^{-}$  derived by Milton et al.<sup>1</sup> yield a ground state splitting of the  $X_1, X_2$  components of 16–20 cm<sup>-1</sup> in the gas phase. The larger splitting is preferred by Pritt *et al.*,<sup>15</sup> who have been able to detect and analyze the contour of the  ${}^{0}P$  branch in the b-X bands of NBr in the gas phase, which involves transitions to  $X_21^{\pm}$ , while only branches involving  $X_1 0^+$  as lower state had been analyzed by Milton et al.<sup>1</sup> The splitting of  $23 \text{ cm}^{-1}$  in site 2 is in good agreement with the gas phase estimates. Further evidence for the correctness of our assignment comes from the temperature dependence of line  $b_2$  in Fig. 5, which is the  $a-X_1$  equivalent of the hot band  $b_1$  in the orbitally allowed  $a - X_2$  transition.

The temperature independent intensities of the lines marked with an asterisk in Fig. 4 (exempting the line in site 1, which was too weak to analyze, see also right-hand panel in Fig. 5), confirm their assignment to the orbitally forbidden  $a-X_1$  transition. There is a third relatively intense line in the spectrum of site 5 in Fig. 4, which is also temperature independent. It is red shifted 10 cm<sup>-1</sup> from the asterisked zpl of the orbitally forbidden  $a-X_1$  zpl at 9161 cm<sup>-1</sup>, and can be assigned to the same electronic transition terminating, however, in the first excited level of a local mode in the  $X_1$  state. The observation of orbitally forbidden transitions due to guest-host interactions is not unprecedented,<sup>6,8,9</sup> and has been previously reported by ourselves.<sup>12</sup> It is, however, important to note that the relaxation of the orbital selection rule is strongly site dependent, which adds support to our assignment of sites 1-5 in Table III: the orbitally forbidden  $a-X_1$  component is strongest in site 2, which puts NBr in a cage of  $C_s$  symmetry. By putting NBr in site 4 of  $C_{2h}$  symmetry, the overall symmetry reduces to  $C_s$ , thus giving rise to the next strongest orbitally forbidden transition in our spectra. The other cages, which lose only some of their symmetry elements when filled with NBr, give rise to less intense orbitally forbidden transitions.

It is not immediately evident why the ground state splitting does not manifest itself in the b-X bands of matrix-isolated NBr. Formulas for calculating rotational line strengths of the b-X transition in the gas phase have been worked out by Watson.<sup>28</sup> Because the Q branch is missing in the gas phase, the transition dipole moment  $\mu_1$  is much smaller than  $\mu_{\parallel}$ , and as a consequence the line strengths of transitions involving  $X_2 1^{\pm}$  as lower level are extremely small for low rotational levels, which are the only ones accessible at low temperatures. Although line strength formulas lose their meaning for the nonrotating matrix-isolated NBr, lack of spin-rotation interaction in the matrix is the reason why  $b0^+ - X_2 1^{\pm}$  transitions are not observed. With our assignment of the a-X spectrum of matrix-isolated NBr we can compare the  $T_0$  values observed in this work with the gas phase. The relevant data for sites 1 and 5 are listed in Table IV. The largest electronic matrix shift, 1.5% for both the b-X and a-X transitions, is found in fcc argon (site 5), which stabilizes the electronically excited states relatively more strongly than do the less symmetric cages in single and multiple stacking faults (hcp pockets).

#### C. Radiative and radiationless relaxation of NBr b $^{1}\Sigma^{+}$

Because a-X emission has been detected in our system, there must be two contributions to the decay rate  $r = 1/\tau$  of the vibrationally relaxed b state: (1) radiative decay with rate  $r_{bX}$  to the electronic ground state, and (2) internal conversion with rate  $r_{ba}$  to the a state. Assuming that the radiative rate is essentially unaffected, the site dependence of process (2) can be estimated from changes of  $r = 1/\tau$  in the b state, and from the intensity ratios  $I_{bX}/I_{aX}$ :

$$I_{bX}/I_{aX} = (r - r_{ba})/r_{ba}.$$

The relevant data are listed in Table V. The intensity ratio  $I_{bX}/I_{aX}$  of site 1 was determined by exciting the (0,0)

TABLE IV. Matrix shifts of the b-X and a-X transitions of NBr in argon.

	$T_0 ({\rm cm}^{-1})$		Matrix		
Transition	gas phase	matrix	in cm <sup>-1</sup>	in %	Refs.
<i>b</i> – <i>X</i>	14 834	14 694ª	140	0.95	1,14
Site 1		14 702.4	132	0.9	This work
Site 5		14 613.9	220	1.50	This work
$a - X_1^{b}$	9281 + 20	$(uncertainty + 10 cm^{-1})$		15	
Site 1		9211 + 23	67	0.7	This work
Site 5		9137 + 25.5	138.5	1.5	This work

<sup>a</sup>Coincides with  $T_0$  of site 2 in this work, cf. Table I.

<sup>b</sup>Given as  $T_0(a - X_1) = T_0(a - X_2) + \Delta E(X_2, X_1)$ .

TABLE V. Site-selective excitation of  $b^{1}\Sigma^{+}$ , v' = 0: intensity ratios of  $b \to X$ and  $a \to X$  emissions as function of site. Intensities  $I_{0,0}$  of the (0,0) bands are given relative to  $I_{bX,00} = 1000$ . Note that  $I_{bX,00}/I_{aX,00}$  was determined indirectly by multiplying the measured ratio  $I_{bX,03}/I_{aX,00}$  of site 1 with the Franck-Condon factor ratio  $q_{00}/q_{03}$  of the b-X system of this site.

Site	$ \begin{array}{c} I_{(0,0)} \\ b \to X_1 \end{array} $	$I_{(0,0)}$ $a \to X_1, X_2$	$I_{b,00}/I_{a,00}$	Lifetime of $b$ state ( $\mu$ s)
1	1000	0.6	1600	39.8 ± 1.4
2	580	0.7	860	$38.7 \pm 0.9$
2′	0	0.8	0	
3	24	1.1	22	$31.5 \pm 1.1$
4	10	1.7	6	30.2 + 1.6
5	980 <sup>a</sup>	2.7	360ª	$34.9 \pm 1.3$

<sup>a</sup> Intensity and intensity ratio uncorrected for increase in Franck-Condon factor ratio  $q_{00}/q_{03}$  from site 1 to site 5.

band at 14 702.4 cm<sup>-1</sup>, while recording the (0,2) band of the b-X transition and the (0,0) band of the a-X transition in one spectral scan (these bands were selected because their intensities are of the same order of magnitude, to match the limited dynamic range of the Varian photomultiplier). The ratio of the band areas was corrected for spectral response, and converted into the intensity ratio of the (0,0) bands, using gas-phase Franck-Condon factors.<sup>15</sup> Intensity ratios  $I_{bx}/I_{ax}$  in other sites were evaluated relative to site 1 from intensity ratios of the lines in Figs. 2(a) and 2(d). The intensity ratios thus obtained are only approximate, because matrix effects on the FCF's<sup>20</sup> were not taken into account. In fact, the intensity ratio of sites 1 and 5 in excitation spectra of the b state was found to vary when the monochromator was tuned to different (0,v'') bands, implying a site dependence of the FCF's.

Internal conversion of the b state to the closest lower vibronic level (v = 7) in the *a* state manifold involves an energy gap of  $\sim 300 \text{ cm}^{-1}$ . This amount of energy must be ultimately converted into bulk phonons of the argon matrix. The process can be mediated by local modes.<sup>29</sup> The coupling should be mainly due to electrostatic guest-host interactions,<sup>30</sup> and is thus likely to depend on the trapping site symmetry, as does the local mode structure of the b-X bands in individual trapping sites, Fig. 3. According to the approximate intensity ratios  $I_{b,00}$  / $I_{a,00}$  listed in Table V, internal conversion from b to a is negligible in the three major trapping sites 1, 2, and 5 (rates  $r_{ba}$  of a few tens of s<sup>-1</sup>), becoming more important in sites 3 and 4. The respective lifetimes, last column in Table V, are accordingly shorter. Only a-Xemission, but no b-X fluorescence, could be detected from site 2', indicating that in this case the rate of internal conversion exceeds the radiative rate of  $2.5 \times 10^4$  s<sup>-1</sup>. This is why we have tentatively assigned sites 2 and 2' to the more likely and less likely orientations of NBr in the  $C_s$  cavity of a single stacking fault (cf. Sec. IV A: orientation of NBr antiparallel and parallel to BA).

The slow vibrational relaxation of the b state in site 5 (as opposed to the much faster vibrational relaxation in sites 1 and 2, cf. Table II and Fig. 7), is in keeping with the enhanced intensity of the (1,1) band relative to the (0,0) band when the laser is tuned to the (1,0) band of site 5. We con-

clude that the coupling of guest vibration with local accepting modes is significantly affected by substitutional site symmetry. Site-dependent vibronic relaxation rates have been previously reported for NCl in argon.<sup>14</sup> The temperature dependence of the vibronic rate in site 5, v' = 1 (filled triangles in Fig. 7) is a common phenomenon,<sup>29,31</sup> and cannot be assigned to a specific mechanism without further information.

There is a striking similarity with respect to the vibrational relaxation rates in the *b* state, of NBr in sites 1 and 2, and NI, which resides in two sites only<sup>12,32</sup>: the rate constants for purely vibrational relaxation in the *b* state are  $k_1 = 0.58 \ \mu s^{-1}$  and  $k_2 = 1.27 \ \mu s^{-1}$  for NBr, slightly less than  $k_1 = 0.63 \ \mu s^{-1}$ ,  $k_2 = 1.68 \ \mu s^{-1}$ , and  $k_3 = 2.53 \ \mu s^{-1}$ for NI. The slower vibrational relaxation of NBr *b*,*v'* ensues from a 10% increase, relative to NI, of the excited state vibrational constant  $\omega_e$ .

### V. SUMMARY AND CONCLUSIONS

Matrix-isolated NBr trapped in two-atom substitutional sites of argon has been excited to the  $b \, {}^{1}\Sigma^{+}$  state. The absorption spectrum of the (0,0) band discloses three major trapping sites. These and two minor sites have also been detected in the fluorescence excitation spectrum of the *b* state. All five sites, plus a sixth site which does not fluoresce in the *b* state, are also detected in spectra of NBr  $a \, {}^{1}\Delta$ . The electronic state, which emits at 1086 nm, is populated via the *b* state by internal conversion. No site scrambling occurs in the process.

A single type of two-atom substitutional site results when two nearest neighbors are removed from a thermodynamically stable fcc argon crystal. Four additional sites of lower symmetry can, however, be created by removing two nearest neighbors from a single stacking fault in a fcc crystal, or from multiple stacking faults (hcp pockets) in solid argon. One of the stacking fault sites has  $C_s$  symmetry, giving rise to effectively two sites, depending on the alignment of NBr in the cavity. It is thus not necessary to invoke impurity effects by  $O_2$  or water, which have been carefully eliminated in this work, in order to explain the heterogeneous structure of the spectra.

Assignments of the spectral features to two-atom substitutional sites of differing symmetry are proposed. The assignments are based on:

(a) the effect of high-temperature annealing, which eliminates all but the thermodynamically most stable site;

(b) probability arguments pertaining to relative abundancies of the sites;

(c) different vibrational relaxation rates in the b state;

(d) site dependence of the  $\Delta \Omega = 0$ ,  $\pm 1$  selection rule in the  $a-X_1$ ,  $X_2$  spectra;

(e) site dependence of the efficiency of internal conversion from  $b^{1}\Sigma^{+}$  to  $a^{1}\Delta$ .

It is suggested that radiationless processes (internal conversion, vibrational relaxation) and orbitally forbidden transitions are enhanced in sites of lower symmetry.

The efficiency of internal conversion in different trapping sites has been evaluated from the intensity ratios of the b-Xand a-X bands in emission. The efficiency was found to vary from <0.1% to near 100%. Several less abundant sites, which are barely detectable in the LIF spectrum of the *b* state, are "amplified" in the *a*-X spectrum by the preference of internal conversion for sites of low symmetry. Trapping site effects have also been helpful in determining the splitting of the  $X_1$ ,  $X_2$  components of NBr in the electronic ground state, which is not known with precision in the gas phase.<sup>15</sup>

In summary, we have shown that matrix effects on "forbidden" radiationless and radiative processes in electronically excited molecules can be strongly affected by the symmetry of the rare gas cage.

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- <sup>32</sup>We have recently measured the absorption spectrum of NI in argon at 5 K (N<sub>2</sub>:I<sub>2</sub>:Ar = 1:1:5000); it compares well with the fluorescence excitation spectra of NI b <sup>1</sup> $\Sigma$ <sup>+</sup> in Ref. 12, confirming our conclusion that only two sites of the radical are important.