PHYSICAL REVIEW B VOLUME 25, NUMBER 4 15 FEBRUARY 1982

EPR measurements of the time dependence of color centers in potassium azide

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(Received 14 July 1981)

Measurements have been made of the amplitudes of EPR signals for N_2^-, NO_2, NO_2^{2-}, and alternate NO_2^{2-} color centers in KN_3 as these color centers develop under irradiation with ultraviolet light. It is found that the buildups of NO_2, NO_2^{2-}, and N_2^- all occur slowly at first, then increase at a rapid rate, and finally approach saturation. Further, they all build at similar rates. The alternate NO_2^{2-}, however, has a different form and buildup rate. Based on the assumption that two excited azide ions interact with nitrate or nitrite impurities, equations have been developed which appear to adequately describe the buildup of NO_2, NO_2^{2-}, and N_2^- color centers, thus indicating that the creation of N_2^- depends on the presence of electron traps and that nitrate and nitrite impurities may provide the needed traps.

I. INTRODUCTION

When potassium azide is irradiated with ultraviolet light from a mercury source (2540 Å), several different color centers are produced which can be detected using electron paramagnetic resonance (EPR) techniques. Colorless samples of this material, irradiated at room temperature or liquid-nitrogen temperature, turn deep lilac in color. If left at room temperature after irradiation, the lilac color fades and the samples appear yellow for an indefinite time. EPR spectra measured at liquid-nitrogen temperatures of samples which had been irradiated at room temperature with ultraviolet light and x rays by Shuskus *et al.*[1] revealed a nine-line spectrum which they associated with an N_4^- defect. The defect is not seen in EPR measurements at room temperature. Horst *et al.*[2] irradiated KN_3 with ultraviolet light at 77 K and identified the same N_4^- defect along with a five-line EPR spectrum which they associated with an N_2^- defect. When the sample was warmed to room temperature and again cooled, the N_2^- center vanished, but not the N_4^-.

Bogan *et al.*[3] have studied the N_4^- and N_2^- defects in some detail using both EPR and optical-absorption techniques. The N_2^- defect seems to anneal at temperatures above 137 K, with some conversion to N_4^-. The latter anneals gradually if left at room temperature.

Owens[4] studied the formation of the N_2^- and N_4^- defects by irradiating samples with polarized ultraviolet light of varying intensities while the samples were in an EPR cavity and held at liquid-nitrogen temperature. He found from his EPR measurements that the formation of the N_2^- defect depended on the excitation of azide ions. He further determined that the initial buildup of N_2^- was slow and proportional to the square of the exposure time and the square of the light intensity. The N_2^- defect concentration then grew rapidly, but eventually saturated (i.e., the growth rate became zero). His illustrations indicate that, for light intensities used, saturation occurred in times less than 200 min. He indicated that no such saturation occurred in the less dominant N_4^- defects. Finally, he indicated that the growth rate of N_2^- was increased in crystals which were less pure and, in particular, was enhanced by the presence of nitrate impurities.

Color centers related to nitrate and nitrite impurities have also been studied in potassium azide. These centers are similarly produced by irradiation with ultraviolet light, but produce observable EPR spectra at room temperature. Mergerian and Marshall[5] reported two defects in this category which they attributed to NO_2 and NO radicals in the material, each producing a three-line spectrum. Fuller and Tarr[6] further studied these defects. They agreed with the NO_2 assignment, but attributed the other spectrum to an NO_2^{2-} defect. They doped their samples with KNO_2 and KNO_3 and determined that NO_2^- is a precursor for both the NO_2 and NO_2^{2-} centers, while NO_3^- is a precursor for NO_2^{2-} only. Willis[7] has reported that, in samples grown from aqueous solutions and irradiated with unfiltered Hg light, the NO_2^{2-} defect is also formed in an alternate orientation.

This study uses EPR measurements to determine the time-dependent buildup of N_2^-, NO_2, NO_2^{2-}, and alternate NO_2^{2-} defects and suggests a model to explain some of the observations.

II. EXPERIMENTAL PROCEDURES

Rectangular platelets of potassium azide were grown by the slow evaporation of an aqueous solution of commercial grade KN_3 (Eastman). The samples were mounted on polystyrene rods and placed in the EPR cavity of a Varian V-4502 EPR Spectrometer in a variable temperature Dewar assembly, except for room-temperature measurements which were made without the Dewar (actually 32 °C due to heating by the uv lamp). The samples were irradiated continuously through a grid in the cavity face with ultraviolet light from an Ultra-Violet Products, Inc. 11 SC 1 lamp with quartz window. The direction of the light was perpendicular to the direction of the spectrometer's magnetic field. The radiation was not filtered and the intensity of the light could not be measured. Samples were of random sizes, though in general they were on the order of 5- to 6-mm square and 1-mm thick. Measurements were made at 170 °C, 100 °C, 32 °C, −35 °C, and −160 °C. During the irradiation, the EPR spectrometer was swept repeatedly over 100 G (2.5 min sweep) or 250 G (5-min sweep) regions about the central field of the pattern. The amplitudes of the EPR signals were considered to be proportional to the concentrations of the defects. The samples, when possible, were oriented so as to prevent or reduce the overlap of the EPR spectral patterns.

III. EXPERIMENTAL RESULTS

Measurements for selected defect peaks of the NO_2, NO_2^{2-}, and alternate NO_2^{2-} defects at 170, 100, and 32 °C are shown in Figs. 1−3. For NO_2 and NO_2^{2-} the curves appear very similar, although different in amplitude. This amplitude difference, based on Fuller and Tarr's[6] work, is probably related to the relative amounts of nitrate and nitrite present in the samples. The curves for NO_2 and NO_2^{2-} are very similar to the N_2^- curves reported by Owens,[4] building up slowly at first, then rising rapidly and eventually appearing to approach saturation. Measurements of NO_2^{2-} shown in Fig. 4 at 32 °C for an extended period of

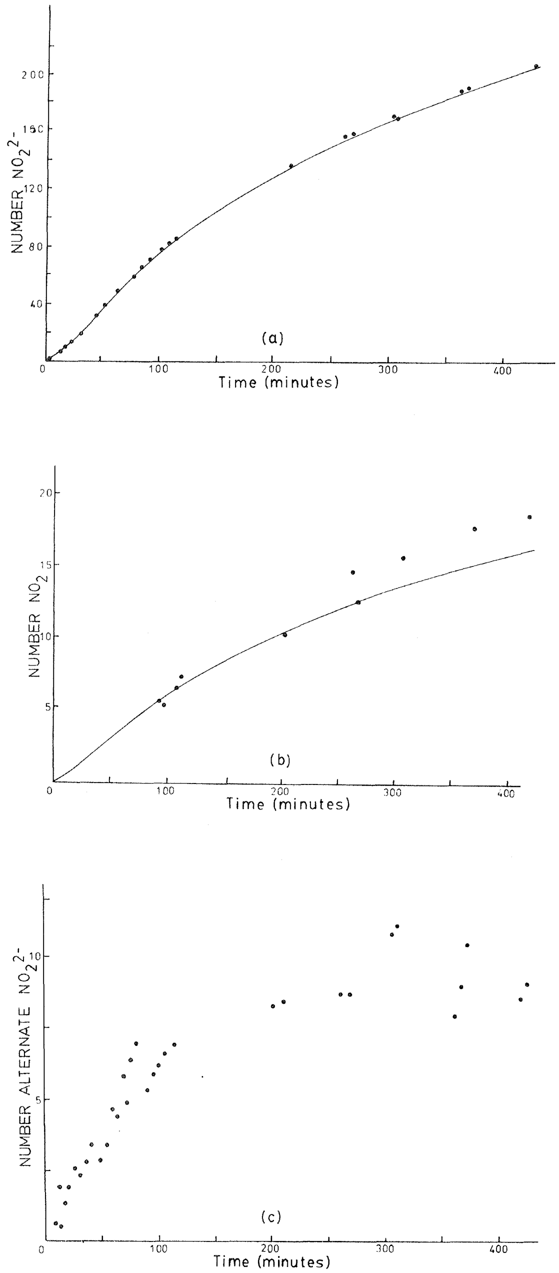

FIG. 1. Densities of color centers in KN_3 as a function of the length of time of uv irradiation at approximately 170 °C (as determined by the measurement of the amplitudes of sample EPR signals). (a) The line is based on the theory of this paper using the amplitude at 200 min and the following values for parameters in the theory: $KI_0^2=8\times10^{-3}$ min^{-1}; $k_5+k_6=2\times10^{-1}$ min^{-1}; $e^{-2\alpha x}=6\times10^{-2}$. (b) Same values are used, with the amplitude again fit at 200 min. The numbers on the vertical axes are arbitrary. They can be used in this figure to measure relative densities but should not be used to compare different numbered figures due to different geometrical setups.

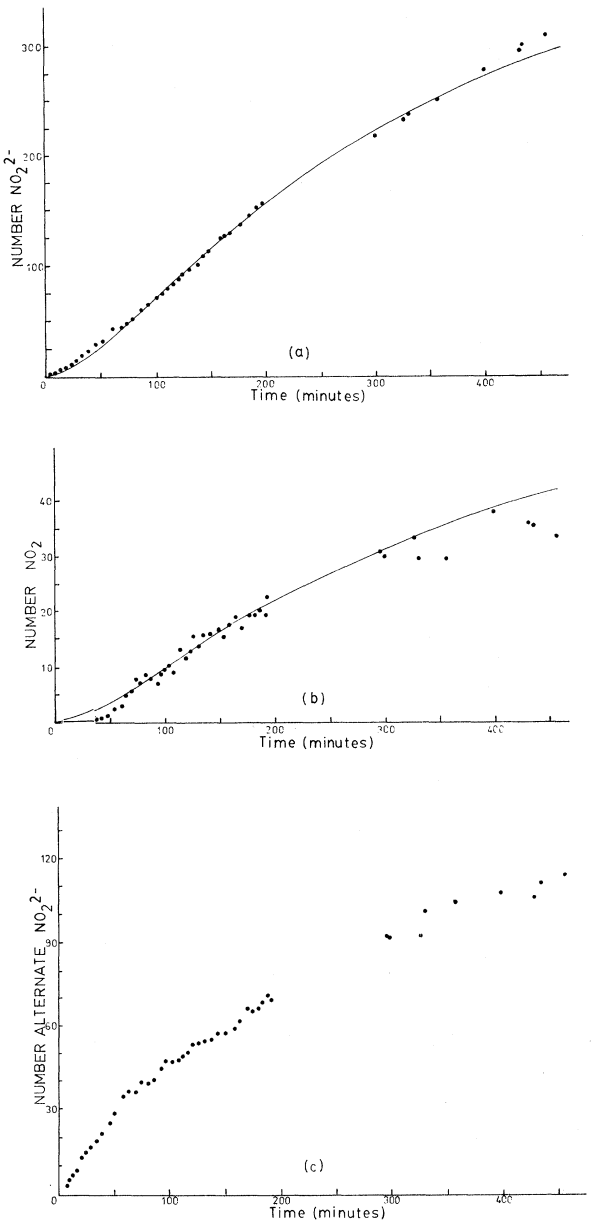

FIG. 2. Densities of color centers in KN_3 as a function of the length of time of uv irradiation at approximately 100 °C. The lines (a) and (b) are drawn as in Fig. 1 with the following values for the parameters: $KI_0^2=8.8\times10^{-3}$ min^{-1}; $k_5+k_6=2.2\times10^{-2}$ min^{-1}; $e^{-2\alpha x}\cong0$ (thick sample). Amplitude is fit at 200 min.

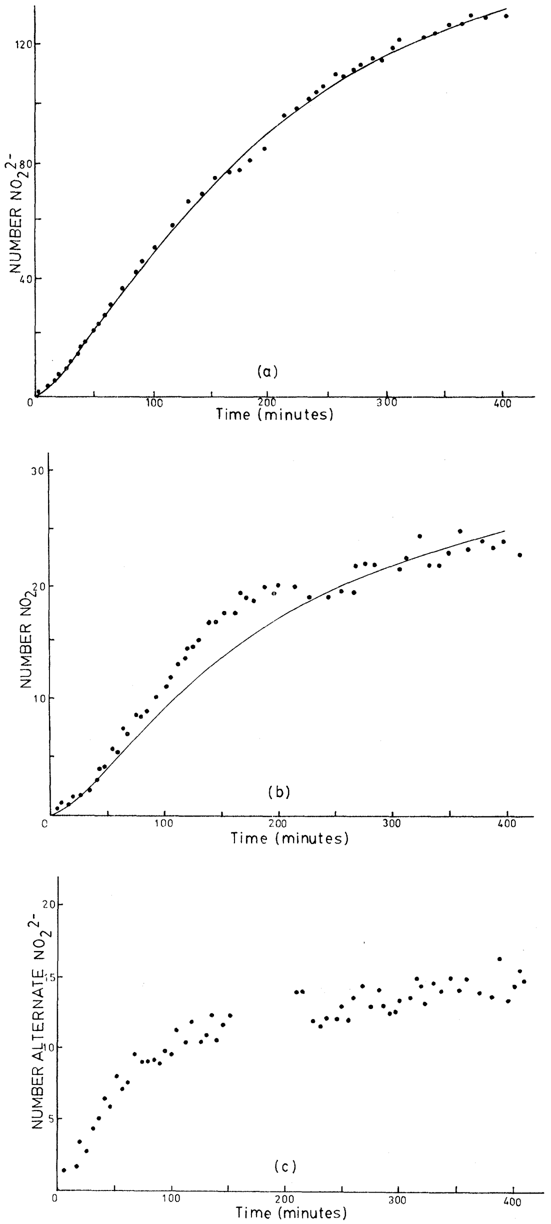

FIG. 3. Densities of color centers in KN_3 as a function of the length of time of uv irradiation at approximately 32 °C. The lines (a) and (b) are drawn as in Fig. 1 with the following values for the parameters: $KI_0^2=1.65\times10^{-2}$ min^{-1}, $k_5+k_6=3.3\times10^{-2}$ min^{-1}; $e^{2\alpha x}=1.5\times10^{-2}$. Amplitude is fit at 100 min.

time indicate that saturation is approached more slowly than is apparent in short-term measurements and that a buildup of defects occurs at a measurable rate for several days. The alternate NO_2^{2-} defect at first builds up more rapidly than NO_2 and NO_2^{2-}. It shows none of the initial time-squared dependence of N_2^-, but does appear to approach saturation. Simultaneous measurements of all of the defects at −160 °C are, unfortunately, virtually impossible to make. NO_2^{2-} and alternate NO_2^{2-} defects are completely overshadowed at all orientations. With the plane of the sample normal to the direction of the light, the N_2^- exhibits a fairly independent pattern. Figure

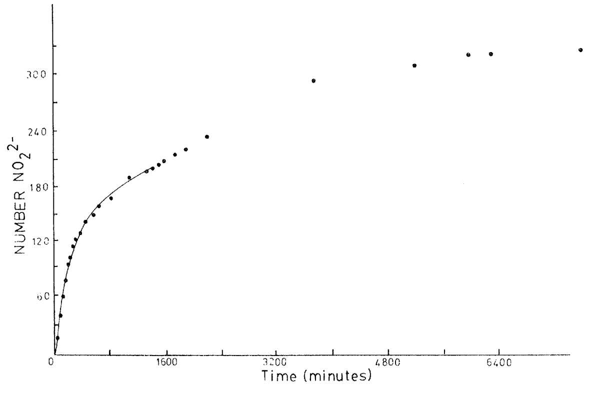

FIG. 4. Data for the NO_2^{2-} color center shown in Fig. 3(a), but plotted for the entire time of irradiation. Later points required a retuning of the EPR system. Since tuning is not exactly reproducible, some scatter of the data points is introduced. Nonetheless, a gradual increase of color center densities over a long time period is demonstrated.

5 is based on measurements in this orientation. It shows a pattern and time dependence very similar to those of NO_2 and NO_2^{2-} at higher temperatures.

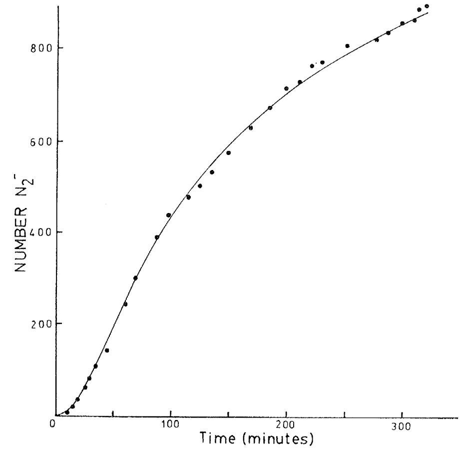

FIG. 5. Density of the N_2^- color center in KN_3 as a function of the length of time of uv irradiation at approximately $-160\,^{\circ}C$. The line is drawn as in Fig. 1(a) with the following values for the parameters: $KI_0^2 = 3\times10^{-2}\ \text{min}^{-1}$; K_5 and $k_6 = 3.45\times10^{-2}\ \text{min}^{-1}$; $e^{-2ax} = 1\times10^{-1}$. Amplitude is fit at 200 min.

IV. DISCUSSION

In his paper on the buildup of the N_2^- defect, Owens[4] suggested that the initial slow buildup and the saturation might not be related to the same impurities. He developed a model to demonstrate a possible explanation of the initial buildup. This model suggests that the growth of $[N_2^-]$ depends on the initial buildup of some other defect $[N_x]$, and that the growth of the two defects might be described by

$$\frac{d[N_2^-]}{dt} = K[N_x][(N_3^-)^*] = k[N_x]I \tag{1}$$

and

$$\frac{d[N_x]}{dt} = aI\ , \tag{2}$$

where I is the intensity of the ultraviolet light. The solution to these equations is

$$[N_2^-] = cI^2t^2\ , \tag{3}$$

where $c = ka/2$.

Owens also reported that the growth of N_2^- occurs only for uv radiation of wavelengths less than 2660 Å. This he related to absorption by the azide ion. Since many experiments have been done irradiating with the 2540-Å light from mercury, Owen's idea would require that either excited azide ions produce both $[N_2^-]$ and $[N_x]$ defects or that both the excited azide ions and the $[N_x]$ defects are produced by the same radiation. The former possibility appears more likely. Although Owens did not require it, it would also be desirable for the same process to produce the saturation effect.

The data presented here for the NO_2 and NO_2^{2-} defects suggests that they are produced by a mechanism similar to that which produces N_2^-. Indeed, the similar rates of buildup for all three of these defects suggest that they may all be related, at least in these impure samples.

Mueller and Singer[8] and Savelyev *et al.*[9] have suggested a variety of ways N_2^- defects might be produced in the photolysis of azides. All suggested processes depend on the presence of a concentration of excited azide ions $[(N_3^-)^*]$.

The simplest monomolecular decompositions suggested are of the following types:

$$(N_3^-)^* \rightarrow N + N_2^-\ , \tag{4}$$

$$(N_3^-)^* \rightarrow N^- + N_2\ . \tag{5}$$

Additionally, $(N_3^-)^*$ might deexcite through a photon or phonon:

$$(N_3^-)^* \rightarrow N_3^- + h\nu\ . \tag{6}$$

Equations (5) and (6) might occur, but the results would not be observable with EPR techniques. Equation (4) does not appear to occur for radiation with ultraviolet light inasmuch as atomic nitrogen has not been detected in EPR spectra.

Bimolecular transformations suggested include

$$2(N_3^-)^* \rightarrow N_6^{2-} \rightarrow N_2^- + N_4^- , \tag{7}$$

$$2(N_3^-)^* \rightarrow N_6^{2-} \rightarrow 2N_2^- + N_2 . \tag{8}$$

These include an intermediate defect as required by Owens,[4] but neither process would explain saturation. Equation (7) also requires $[N_2^-]$ and $[N_4^-]$ to grow at the same rates, a result not observed by Owens. Savelyev *et al.*[9] also suggested several processes involving traps:

$$2(N_3^-)^* + T \rightarrow (N_6^{2-} \cdot T)^*$$

$$\rightarrow N_2^- + T \cdot e + 2N_2 , \tag{9}$$

or

$$\rightarrow N_4^- + T \cdot e + N_2 , \tag{10}$$

or

$$\rightarrow 3N_2 + T \cdot e \cdot e . \tag{11}$$

These reactions fit the requirement for an intermediate defect (shown in parentheses). Limitations caused by the number of traps could explain the saturation. Savalyev *et al.* have reported that in alkali azides, after photolysis, there is a dark liberation of N_2 which quadratically depends on the intensity of the previous radiation. Nitrogen is indeed produced by the above equations. The trapped electron might or might not be detected by EPR techniques. Since it has been noted that the presence of nitrates enhances the production of N_2^-, we suggest the possibility of a trap mechanism similar to that suggested by Savelyev *et al.* being either a nitrate or a nitrite. This suggestion would lead to the following possible reactions.

Single $(N_3^-)^*$ (monomolecular):

$$(N_3^-)^* + NO_2^- \rightarrow (N_3^- \cdot NO_2^-)^*$$

$$\rightarrow NO_2^{2-} + \underline{N_3^0} , \tag{12a}$$

or

$$\rightarrow NO_2^{2-} + N_2 + \underline{N} , \tag{12b}$$

or

$$\rightarrow NO_2 + \underline{N_3^{2-}} , \tag{13}$$

and

$$(N_3^-)^* + NO_3^- \rightarrow (N_3^- \cdot NO_3^-)^*$$

$$\rightarrow NO_2^{2-} + \underline{NO} + N_2 , \tag{14}$$

or

$$\rightarrow NO_2^{2-} + N_2O + \underline{N} . \tag{15}$$

(The underlined radicals are paramagnetic species which have not been observed.)

Two $(N_3^-)^*$ (bimolecular) (inasmuch as I do not know the geometry of the intermediate complex, I have written it with $2N_3^-$ instead of N_6^{2-} as used by Savelyer *et al.*):

$$2(N_3^-)^* + NO_2^- \rightarrow (2N_3^- \cdot NO_2^-)^*$$

$$\rightarrow N_2^- + NO_2^{2-} + 2N_2 , \tag{16}$$

or

$$\rightarrow N_4^- + NO_2^{2-} + N_2 , \tag{17}$$

or

$$\rightarrow 3N_2^- + NO_2 , \tag{18}$$

and

$$2(N_3^-)^* + NO_3^- \rightarrow (2N_3^- \cdot NO_3^-)^*$$

$$\rightarrow N_2^- + NO_2^{2-} + N_2O + N_2 , \tag{19}$$

or

$$\rightarrow N_4^- + NO_2^{2-} + N_2O . \tag{20}$$

These equations meet the criteria of an intermediate defect and the requirement for saturation based on a limited number of nitrate and nitrite ions. They have been written to agree with Fuller and Tarr[6] in that nitrite is a precursor to both NO_2 and NO_2^{2-}, while nitrate is a precursor to NO_2^{2-} only. Since Owens reported that N_4^- does not saturate, we will not consider equations in which it is a product.

Based on these equations and some assumptions listed below, an equation can be developed to describe the buildup of the defects with respect to time and intensity. To simplify the discussion we will consider that only nitrite impurities are present and a bimolecular process occurs following both Eq. (16) and (18). We will further assume that Eq. (6) represents by far the most probable reaction involving excited azide ions. All other reactions, including Eqs. (16) and (18), are almost negligible in comparison. We finally consider that all azide ions have an equal probability of excitation by the incoming ultraviolet light of intensity I such that the density of excited ions increases as follows:

$$\frac{d[(N_3^-)^*]}{dt}=k_1 I , \tag{21}$$

where k is a constant of proportionality and square brackets represent ion densities. In the following equations, k is a rate constant. Based on chemical kinetics the density of excited azide ions decreases according to Eqs. (6), (16), and (18) as follows:

$$\begin{aligned}-\frac{d[(N_3^-)^*]}{dt}&=k_2[(N_3^-)^*]\\&\quad+k_4[(N_3^-)^*]^2[NO_2^-]\\&\quad+k_3[\cdots] ,\end{aligned} \tag{22}$$

where the ellipses represents other possible reaction terms. If Eq. (6) represents the dominant reaction, then as an approximation Eq. (22) can be simplified to read

$$-\frac{d[(N_3^-)^*]}{dt}=k_2[(N_3^-)^*] . \tag{23}$$

When equilibrium is achieved, (21) and (23) can be equated, yielding for any time,

$$[(N_3^-)^*]=\frac{k_1}{k_2}I , \tag{24}$$

the requirement suggested by Owens.[4]

In discussing the kinetics of Eqs. (16) and (18), we will use the letter C to represent the intermediate complex,

$$C=(2N_3^-\cdot NO_2^-)^* . \tag{25}$$

The formation rate for C is the same as the rate NO_2^- impurities in the material are used in reactions (16) and (18). Thus,

$$\begin{aligned}-\frac{d[NO_2^-]}{dt}=\frac{d[C]}{dt}&=k_4[(N_3^-)^*]^2[NO_2^-]\\&=k_4\left[\frac{k_1}{k_2}\right]^2 I^2[NO_2^-]\\&=KI^2[NO_2^-] ,\end{aligned} \tag{26}$$

where we have replaced the small k's with one constant K. The rate constants for the dissociation of C via routes (16) and (18) are given the symbols k_5 and k_6. Thus, the net rate of change of C is given by

$$\frac{d[C]}{dt}=KI^2[NO_2^-]-(k_5+k_6)[C] , \tag{27}$$

and the buildup of NO_2^{2-} is given by

$$\frac{d[NO_2^{2-}]}{dt}=k_5[C] . \tag{28}$$

Solving (26), (27), and (28) together yields

$$\begin{aligned}[NO_2^{2-}]=&\frac{Z}{KI^2}(1-e^{-KI^2t})\\&-\frac{Z}{(k_5+k_6)}(1-e^{-(k_5+k_6)t}) ,\end{aligned} \tag{29}$$

where

$$Z=\frac{k_5[NO_2^-]_0 KI^2}{k_5+k_6-KI^2} , \tag{30}$$

and where $[NO_2^-]_0$ is the initial concentration of nitrite impurities. Similar relationships can be developed for the other paramagnetic radiation products.

Equation (29) assumes the uv light intensity is constant through the sample. As Owens[4] indicates, the uv light is actually strongly absorbed. Equation (21) implies that for light moving in the x direction through the material,

$$I(x)=I_0 e^{-\alpha x} , \tag{31}$$

where I_0 is the incident light intensity and α is a linear absorption coefficient. For the samples we are using, we need to substitute (31) into (29) and integrate over the thickness of the sample. This results in the following series solution:

$$\begin{aligned}[NO_2^{2-}]=\frac{M}{2\alpha}\Bigg\{&\Bigg[\frac{g^2}{2!}-\frac{g^3}{3!}\left[b+\frac{1}{2}\right]+\frac{g^4}{4!}\left[b^2+\frac{b}{2}+\frac{1}{3}\right]-\frac{g^5}{5!}\left[b^3+\frac{b^2}{2}+\frac{b}{3}+\frac{1}{4}\right]+\cdots\Bigg]\\&-e^{2\alpha x}\left[\frac{G^2}{2!}-\frac{G^3}{3!}\left[B+\frac{1}{2}\right]+\frac{G^4}{4!}\left[B^2+\frac{B}{2}+\frac{1}{3}\right]-\cdots\right]\Bigg\} ,\end{aligned} \tag{32}$$

where

$$M=\frac{k_5[\mathrm{NO_2}^-]_0}{KI_0^2}\ , \tag{33}$$

$$g=KI_0^2t\ , \tag{34}$$

$$b=\frac{k_5+k_6}{KI_0^2}\ , \tag{35}$$

$$G=ge^{-2\alpha x}\ , \tag{36}$$

$$B=be^{2\alpha x}\ , \tag{37}$$

and x is the thickness of the sample.

For short periods of time the first term of this series dominates, such that

$$[\mathrm{NO_2}^{2-}]=\frac{\mathrm{k}_5[\mathrm{NO_2}^-]_0}{2!2\alpha}KI_0^2t^2$$

$$=(\mathrm{const})I_0^2t^2\ , \tag{38}$$

in agreement with Owens's[4] findings for the $\mathrm{N_2}^-$ defect. Further, we find that the value of $[\mathrm{NO_2}^{2-}]$ over long periods of time saturates, approaching

$$\frac{k_5}{k_5+k_6}[\mathrm{NO_2}^-]_0\ . \tag{39}$$

This can be seen more easily from Eq. (29) than from (32), the latter being a sum of the former for different intensities as we proceed through the material. The solid lines in the various figures are attempts to fit theory to data. They are based in Figs. 1(a), 2(a), 3(a), and 5 on attempts to fit the buildup of $\mathrm{NO_2}^{2-}$ and $\mathrm{N_2}^-$ using K, k_5+k_6, and $e^{-2\alpha x}$ as variables and trying to fit a single point, usually at 200 min. Although fairly good fits could be made for initial time periods, the theoretical curves tended to approach saturation too soon. It is unreasonable, however, to expect a better fit. The theory assumes a smooth infinite plate of material of uniform thickness. The samples used were finite and edge effects were present. Surfaces were not smooth resulting in nonuniform refraction. Finally, the thickness was not uniform. Thicker areas would reach saturation later than the thinner areas and keep the defects building up for a long time.

For a given sample, considering Eqs. (16) and (18), the parameters used for $\mathrm{NO_2}^{2-}$ should also describe the buildup of $\mathrm{NO_2}$. Figures 1(b), 2(b), and 3(b) show attempts to hit $\mathrm{NO_2}$ data with the same parameters. The results show limited success but it should be noted that nitrates are also probably present and that reaction (19) is also probably contributing to the buildup of $\mathrm{NO_2}^{2-}$. Thus, all we can expect is a general agreement of shape and that is exhibited. The buildup of $\mathrm{N_2}^-$ also exhibits the same general shape and rate constants and so it is not unreasonable to assume that Eqs. (16), (18), and (19) may be valid.

As seen in Figs. 1(c), 2(c), and 3(c), the buildup of the alternate $\mathrm{NO_2}^{2-}$ does not exhibit an initial buildup proportional to time squared and intensity squared, or it occurs so quickly it is not observable with the equipment used. Thus, the formation of these color centers appears to result from a different reaction process, perhaps the simple trapping of an electron by a nitrite impurity or perhaps through some alternate complex or alternately configured complex which dissociates more rapidly than that already discussed. If this does involve nitrite ions, it represents another process competing with (16) and (18) and would appropriately also have to be included in the chemical kinetics.

V. CONCLUSION

Based on previous observation (Owens[4]) of the buildup of $\mathrm{N_2}^-$ defects in $\mathrm{KN_3}$ and the observations of the authors, it appears that equations can be developed for this buildup with the appropriate time and light dependence by assuming the interaction of two excited azide ions with an electron trap. The buildups of $\mathrm{NO_2}^{2-}$ and $\mathrm{NO_2}$ defects seem to have the same type of time dependence as that of the $\mathrm{N_2}^-$ and can be described by the same equations and very similar rate constants. It appears probable, therefore, that nitrite and nitrate impurities provide traps which are involved in the formation of $\mathrm{N_2}^-$ defect color centers in $\mathrm{KN_3}$.

ACKNOWLEDGMENT

Work for this paper was supported by the U.S. Army Research Office, Durham, North Carolina.

[*] Currently serving in the U.S. Army.

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