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Infrared Spectrum of Propynyl Boron Difluoride*

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Propynyl boron difluoride, CH₂C≡CBF₂, has been synthesized for the first time and its infrared spectrum determined over the 4000-250-cm⁻¹ region. All 20 fundamentals have been assigned based on band shape considerations, characteristic group frequencies, or isotopic splitting. The gas phase spectrum was compatible with a molecular model belonging to the G_{12} symmetry group for nonrigid structures. Resolved Q-branch structure was observed for the asymmetric methyl stretching fundamental $\nu_8(e')$ which resulted from the freely rotating methyl group. The Coriolis coupling coefficient for this mode was estimated to be $\zeta_8 = +0.16$.

Propynyl boron difluoride, $CH_3C=CBF_2$, is an example of a molecule containing an acetylenic bond which separates two functional groups, one being a symmetric rotor and the other an unsymmetrical framework. Molecules of this general type are of considerable theoretical interest because they are characterized by very low barriers to internal rotation whose values can be determined using either microwave or high-resolution infrared spectroscopy.

Since $CH_3C\equiv CBF_2$ is a previously unknown compound, its structure and spectrum are of some importance. This paper presents a complete vibrational assignment of this molecule based on its infrared spectrum. The only other known members of the alkynyl dihaloboranes are the ethynyl boron dihalides, $HC\equiv CBX_2$ (X=F, Cl), whose synthesis and structure were reported recently.^{1,2}

EXPERIMENTAL

Propynyl boron difluoride was prepared by allowing a gaseous reaction mixture containing BF₂Cl to react with solid dipropynyl mercury, $(CH_3C \equiv C)_2Hg$, in vacuo. The BF₂Cl reactant was obtained from a 2:1 mixture of BF₃ and BCl₃ in which BF₂Cl forms as an independent molecular species.³ Dipropynyl mercury was obtained by dropwise addition of an aqueous K₂HgI₄ solution to water that was continuously saturated with methyl acetylene, followed by filtration and sublimation of the reaction product.⁴ The principal reaction was carried out by very slowly passing 0.15 g of the above boron trihalide mixture through a small diameter glass tube containing approximately 0.40 g dipropynyl mercury. The ensuing reaction was rapid and exothermic, and since only a few tenths of a millimole of products were produced, it was necessary to run several such reactions in succession. Upon condensing all the crude product into a U tube trap of a vacuum system, the CH₃C≡CBF₂ was isolated from the impurities by simple fractionation from a U tube cooled to -55° C. Vapors emanating from this trap were passed through another U tube cooled to -89° C and into a third U tube at -196°C. Nearly pure CH₃C≡CBF₂ condensed in the -89°C trap, while unreacted boron trihalides and methyl acetylene were condensed in the -196° C trap. Other impurities remained in the -55° C trap. The purest samples of CH₃C \equiv CBF₂ were obtained by a second redistillation of the material in the -89° C U tube. Identity and purity of the CH₃C \equiv CBF₂ samples were established from infrared and mass spectra. A survey infrared spectrum of CH₃C \equiv CBF₂ is shown in Fig. 1.

During this investigation it was found that $CH_3C\equiv CBF_2$ could be obtained by two other reactions, in addition to the method described above. For example, if a 2:1 mixture of BF_3 and BBr_3 were allowed to react with dipropynyl mercury, $CH_3C\equiv CBF_2$ was formed in low yield. It was also found that the previously unknown molecule, $CH_3C\equiv CBCl_2$, could be prepared in 25% yield by the reaction of BCl_3 with dipropynyl mercury. Upon fluorinating $CH_3C\equiv CBCl_2$ with SbF_3 at $-45^{\circ}C$, propynyl boron difluoride was formed in low yield. Propynyl boron difluoride proved to be a reactive and somewhat chemically unstable molecule at ambient temperatures. As a result, even though freshly distilled samples were investigated at all times, traces of BF_3 were found in the infrared spectra.

The melting point of CH₃C \equiv CBF₂ was $-61.3\pm0.5^{\circ}$ C, as measured by the magnetic plunger method.⁵ Vapor pressure data for liquid CH₃C \equiv CBF₂, determined over the 215-260°K temperature interval, fit the equation, $\log_{10}P(\text{torr}) = -1622.8/T + 8.628$, from which the normal boiling point of CH₃C \equiv CBF₂ was estimated to be 282°K, and the heat of vaporization was 7.43 kcal/mole.

The infrared spectrometers used in this investigation were a Perkin–Elmer model 21 with NaCl optics to monitor sample purity, and a Perkin–Elmer model 16 single beam grating spectrometer which has been described elsewhere.⁶ The grating instrument was calibrated with vibration–rotation spectra of simple gases,⁷ or the pure rotational spectrum of water vapor.⁸ The measured wavenumbers of the band centers are thought to be accurate to ± 1 cm⁻¹, except in those regions where the absorptions were overlapped. Pyrex gas cells of 10-cm path length with alkali halide windows were used to obtain the vapor phase results, while polycrystalline thin film spectra at liquid nitrogen temperature were obtained with a conventional glass low temperature cell. A Spex model 1401 Raman spectrometer equipped



FIG. 1. Low-resolution infrared spectrum of $CH_3C=CBF_2$ (A=55 torr, B=10 torr, C=3 torr). The path length was 10 cm.

with a Ar^+/Kr^+ laser was employed in several unsuccessful attempts to measure the Raman spectrum of $CH_3C\equiv CBF_2$. The samples either decomposed in the laser beam at room temperature, or fluoresced to such an extent with a Harney-Miller low temperature cell that a satisfactory Raman spectrum could not be obtained.

SPECTRAL RESULTS AND DISCUSSION

Chemically speaking, the most realistic model to assume for $CH_3C \equiv CBF_2$ is that the CH_3 and BF_2 groups, which are bonded to opposite ends of an acetylenic functional group, rotate freely with respect to each other. Free internal rotation was assumed, since insertion of an acetylenic group between two axially bonded functional groups is known to diminish significantly the barrier to internal rotation in a molecule. The essential correctness of the assumption of free internal rotation for $CH_3C \equiv CBF_2$ is supported by the fact that the measured barrier for CH₃BF₂ is only 13.77 cal/mole.⁹ Since microwave data are not presently available for CH₃C=CBF₂, bond angles and distances had to be estimated from geometries of structurally related molecules. From the molecular parameters of CH₃C=CH¹⁰ and HC=CBF₂² the rotational constants for $CH_3C \equiv CBF_2$ were estimated to be: A = 0.330, B=0.051, and C=0.045 cm⁻¹. From these values the asymmetry parameter, κ , was estimated to be -0.96, suggesting that $CH_3C \equiv CBF_2$ is a near prolate symmetric top molecule.

Because CH₃C=CBF₂ was assumed to have a zero barrier to internal rotation, its vibrational modes were most accurately represented by a symmetry group for nonrigid molecules, such as have been discussed by Longuet-Higgins,¹¹ and others.^{12–14} Propynyl boron difluoride belongs to Longuet-Higgins' G_{12} symmetry group which possesses 12 symmetry elements and is isomorphous with the more familiar D_{3h} point group. To determine the vibrational representation for this molecule it must be recognized that for a molecule with a single free rotor there will be 3N-7 normal modes of vibration. Since CH₃C=CBF₂ is a nine-atom molecule, there are 20 normal modes. Also, each normal mode of vibration is well represented by a symmetry coordinate of the molecule, which in turn reflects the symmetry of one of the irreducible representations of the G_{12} symmetry group. Accordingly, symmetry coordinates were generated for CH₃C=CBF₂ by the usual group theory methods and after removing the redundant coordinates, the vibrational representation emerged as $\Gamma_{vib} = 7A' + 5E' + 2A_1'' + A_2''$ with all fundamentals being infrared active.

Treating the rotational problem next, for rigid molecules the theoretical aspects of the problem are well defined; however for molecules with free internal rotation there is a complication due to the additional degree of rotational freedom. Jones and Sheppard¹⁵ have treated the CH₃XY₂-type molecule in detail and an extension of their analysis to CH₃C=CBF₂ has proven to be acceptable. To a first approximation the rotational energy levels of the methyl group in CH₃C=CBF₂ are represented by

$$F(J, K, k_1) = DJ(J+1) + A_1k_1^2 + (A_2 - D)(K^2 - dKk_1) \text{ cm}^{-1}, \quad (1)$$

where J and K have their usual significance, and k_1 denotes the quantum number corresponding to angular momentum of the methyl group about the axis of internal rotation. The other quantities in Eq. (1) are

$$D = (B+C)/2,$$

$$A_1 = hI_A/8\pi^2 I_\alpha (I_A - I_\alpha)c,$$

$$A_2 = h/8\pi^2 (I_A - I_\alpha)c,$$

$$d = 2A_2/(A_2 - D),$$

where I_{α} denotes the moment of inertia of the methyl group about the axis of internal rotation. Selection rules were developed for the perpendicular normal modes, since rotational structure was expected for these infrared bands only. The selection rules for the most likely transitions of the methyl rotor are $\Delta J=0, \pm 1$, $\Delta K=\pm 1$, and $\Delta k_1=\pm 1$, which may be shown to reflect the symmetry of the E' irreducible representation.

Applying the selection rules to Eq. (1) gave the following expression for the wavenumbers of the Q branch transitions for the degenerate perpendicular methyl

=

vibrations

$$\nu = \nu_0 + A_1 + (A_2 - D) (1 - d) \pm [2A_1 - d(A_2 - D)] |k_1| \\ \pm (A_2 - D) (2 - d) K \operatorname{cm}^{-1}, \quad (2)$$

where v_0 represents the band origin, and the plus sign designates the ${}^{R}Q_{k_{1}}$ transitions arising from $\Delta |k_{1}| = +1$, while the minus sign depicts the PQ_{k_1} transitions for $\Delta |k_1| = -1$. Transitions associated with $\Delta J = \pm 1$ were not considered, since they contribute only to the unresolved background of the bands with the spectrometers used in this study. It has been shown¹⁵ that the most intense transitions of any given Q branch are associated with K values of $K = d |k_1|/2$ which causes Eq. (2) to become

$$\nu = \nu_0 + A_1 + (A_2 - D) (1 - d)$$

$$\pm [2A_1 - d^2(A_2 - D)/2] |k_1| \text{ cm}^{-1}. \quad (3)$$

Two additional considerations must next be incorporated into Eq. (3): These are the difference in the upper



3000 WAVENUMBERS (cm⁻¹)

2900

P=150 torr

3100

and lower state rotational constants and Coriolis interactions. For a true symmetric top the difference in the upper and lower state rotational constants appears in the equation for the Q branches as a coefficient of K^2 . By analogy, for CH₃C=CBF₂ this difference, which was associated with changes in A_1 , was incorporated in Eq. (3) as a term in k_1^2 . Since the vibrational transitions of the methyl group under consideration were from a nondegenerate ground state to a degenerate upper state, Coriolis interactions in the degenerate state were approximated. By analogy with other work¹⁵ the effect of Coriolis interaction resulted in Eq. (3)becoming

$$\nu = \nu_0 + 5.104(1 - \zeta_i^2) \pm 10.193(1 - \zeta_i) |k_1| + (A' - A'')k_1^2 \,\mathrm{cm}^{-1} \quad (4)$$

when numerical values for the various terms of Eq. (3)were inserted. In Eq. (4) the prime and double prime quantities refer to the upper and ground states, respectively, and ζ_i is the Coriolis coupling constant.

TABLE I. Q-branch wavenumbers (cm^{-1}) for $\nu_8(e')$ of CH₄C≡CBF₂.

	$^{R}Q_{k_{1}}$		PQ_{k_1}		
k 1	Obs	Calc	Obs	Calc	
0	3019.7	3019.5			
1	3029.1	3029.0	3009.8	3009.7	
2	3038.5	3038.4	3000.1	3000.0	
3	3047.8	3047.7	2989.4	2989.8	
4	3056.3	3056.8	2979.2	2979.7	
5	3065.6	3065.7	2968.9	2969.3	
6	3074.7	3074.5	2959.0	2958.8	

For all other normal vibrations of $CH_3C \equiv CBF_2$ where $\Delta k_1 = 0$, type-A, B, or C infrared band contours typical of asymmetric top molecules were predicted. Those modes associated with dipole moment changes along the smallest inertial axis would be expected to give rise to type-A infrared bands with POR-branch structure. Those modes having dipole moment changes along the largest inertial axis should give rise to type-C infrared bands characterized by a strong central O branch and weaker P and R branches, while the modes with dipole changes along the intermediate inertial axis were predicted to cause type-B infrared bands with prominent P and R branches and no Q branch. The separation between maxima of the various bands was calculated by the method of Seth Paul and Disjkstra.¹⁶ The P-Rseparation at 300°K for an A-type band was estimated to be 10.1 cm⁻¹, for a B-type band 8.4 cm⁻¹, and for a C-type band 15.1 cm⁻¹.

CH₃ Group Vibrations

Since the normal modes of vibration for CH₃C=CBF₂ are adequately characterized in terms of functional group vibrations, the observed infrared spectrum can be conveniently treated in terms of CH₃ group vibrations, BF₂ group vibrations, or skeletal vibrations.

There was little doubt about the assignment of the doubly degenerate CH₃ asymmetric stretch, $\nu_8(e')$, which is shown in Fig. 2 as the set of resolved O branches in the 2960-3080-cm⁻¹ region. The intensity alternation

FIG. 3. The BF₂ symmetric and asymmetric stretching modes of $CH_3C \equiv CBF_2$. The path length was 10 cm and the spectral slitwidth was 0.4 cm⁻¹.







FIG. 6. The BF_2 in-plane rock of $CH_3C=CBF_2$. The path length was 10 cm and the spectral slitwidth was 0.4 cm⁻¹.

permitted the *Q* branches to be assigned in a straightforward manner and the observed wavenumbers are listed in Table I. By employing sum and difference relationships the equations for the observed *Q*-branch transitions are

$${}^{R}Q_{k_{1}} + {}^{P}Q_{k_{1}} = 6037.59 - 0.1420k_{1}{}^{2} \text{ cm}^{-1},$$

 ${}^{R}Q_{k_{1}} - {}^{P}Q_{k_{1}} = 19.15 \mid k_{1} \mid \text{cm}^{-1}.$

This caused Eq. (4) to read

$$\nu = 3018.80 \pm 9.58 | k_1 | - 0.0710 k_1^2 \text{ cm}^{-1}$$

from which it followed that $\zeta_8 = +0.16$, $\nu_0 = 3014.3$ cm⁻¹, and A'-A''=-0.0710 cm⁻¹. It is possible that the additional transition at 2991.3 cm⁻¹ was a hot band.

The other degenerate methyl vibrations of $CH_3C \equiv$ CBF₂, the asymmetric CH₃ deformation, $\nu_9(e')$, and the CH₃ rock vibration, $\nu_{10}(e')$, were not observed in the gas-phase infrared spectrum. The CH₃ deformation was obscured by the very intense BF2 stretching absorptions in the 1350-1450-cm⁻¹ region, but a reasonable estimate of its fundamental frequency was obtained from its first overtone which occurred at 2874 cm⁻¹, in Fermi resonance with $\nu_1(a_1')$. The CH₃ rocking mode was either too weak to be observed in the gas-phase spec-



WAVENUMBERS

(cm⁻¹)

FIG. 5. The BF₂ scissors mode of CH₃C≡CBF₂. The path length was 10 cm and the spectral slitwidth was

0.4 cm⁻¹.

TABLE II. Infrared wavenumbers (cm⁻¹) for CH₃C=CBF₂.

trum or was obscured by the C-C stretch, $\nu_5(a_1')$, at

1018.5 cm⁻¹; however, from a low-temperature poly-

crystalline thin-film spectrum an absorption at 1022

cm⁻¹ was observed which was assigned to the CH₃ rock.

Wavenumber	Assignment	Approximate normal mode		
3014.3	$\nu_8(e')$	CH ₃ asymmetric stretch		
2944 R				
2938.6 Q	$\nu_1(a_1')$	CH ₃ symmetric stretch		
2933 P	· - <i>i</i>			
2874	$2\nu_9(A_1'+E')$			
2421	$\nu_{13} + \nu_5(A_1'')$			
2337	$\nu_4 + \nu_5(A_1')$			
2228	$\nu_2(a_1')$	C=C stretch		
1437 ª	$v_9(e')$	CH ₃ asymmetric deformation		
1428				
1417	$\nu_{13}(a_1'')$	¹⁰ BF ₂ asymmetric stretch		
1378 ^b	$\nu_{3}(a_{1}')$	CH ₃ symmetric deformation		
1377				
1369	$\nu_{13}(a_1'')$	¹¹ BF ₂ asymmetric stretch		
1344 R		- 2		
1339.6 <i>0</i>	$v_4(a_1')$	¹⁰ BF ₂ symmetric stretch		
1333 P	,			
1333 R				
1328.3 Q	$\nu_4(a_1')$	¹¹ BF ₂ symmetric stretch		
1323 P				
1022ь	$v_{10}(e_1')$	CH₃ rock		
1021 R				
1018.5 Q	$v_5(a_1')$	C–C stretch		
1012 P				
782	$\nu_6(a_1')$	C–B stretch		
747	$2\nu_{12}(A_1'+E)$			
665.5	$v_{15}(a_2'')$	BF ₂ out-of-plane wag		
600	$2\nu_{14}(A_1')$			
499	$v_7(a_1')$	BF ₂ scissors		
406	$v_{11}(e')$	C≡C-B bend		
371	$v_{12}(e')$	C−C≡C bend		
307	$\nu_{14}(a_1'')$	BF ₂ in-plane rock		

* Estimated from first overtone.

^b Obtained from low-temperature polycrystalline thin film.

<i>T</i> (°K)		C_p°/R	$(H^{\circ}-H_{0}^{\circ})/RT$	$-(G^{\circ}-H_{0}^{\circ})/RT$	S°/R	
	Translation	2.50	2.50	17.29	19.79	
	Rotation	1.50	1.50	12.16	13.66	
298.16	Vibration	5.87	2.30	1.04	3.34	
	Int. rot.	0.50	0.50	0.60	1.10	
		10.37	6.80	31.09	37.89	
400		12.48	7.98	33.26	41.24	
500		14.21	9.06	35.16	44.22	
600		15.64	10.04	36.90	46.94	
700		16.82	10.93	38.51	49.44	
800		17.80	11.73	40.02	51.75	
900		18.63	12.45	41.45	53.90	
1000		19.33	13.10	42.79	55.90	

TABLE III. Thermodynamic properties for CH₃C=CBF₂.

The two remaining methyl group vibrations are the symmetric CH₃ stretch, $\nu_1(a_1')$ and the symmetric CH₃ deformation, $\nu_3(a_1')$, which were assigned as follows. The symmetric CH₃ stretch appeared as a well-defined type-A band at 2938.6 cm⁻¹, with an observed P-R separation of 11 cm⁻¹ which agreed well with the calculated value of 10.1 cm⁻¹. The $\nu_3(a_1')$ absorption was obscured by the BF₂ absorptions and was not so readily assigned. From a polycrystalline thin film spectrum $\nu_3(a_1')$ was assigned to an absorption at 1378 cm⁻¹.

BF₂ Group Vibrations

The BF₂ stretching vibrations are shown in Fig. 3 where the effect of isotopic splitting may be clearly seen. The weakest absorption in this scan is a doublet centered near 1422 cm⁻¹ which was assigned to the ¹⁰BF₂ asymmetric stretch, $\nu_{13}(a_1'')$, while the stronger doublet centered at 1373 cm⁻¹ was taken to be the corresponding mode of the ¹¹BF₂ group. The BF₂ symmetric stretch, $\nu_4(a_1')$, was also split by isotopic substitution with the two bands being partially overlapped. The Q branch of the ¹⁰BF₂ vibration was taken to be at 1339.6 cm⁻¹, while that for the ¹¹BF₂ vibration was at 1328.3 cm⁻¹.

The other BF₂ vibrations all absorbed at lower wavenumbers. The BF₂ out-of-plane wag, $\nu_{15}(a_2'')$, occurred as a type-C band with a prominent Q branch at 665.5 cm⁻¹ and is shown in Fig. 4. The additional absorptions at 691.5 and 719.0 cm⁻¹ in this figure were caused by traces of BF₃ impurity. The BF₂ scissors, $\nu_7(a_1')$, occurred at 499 cm⁻¹ based on wavenumbers for the analogous vibrations of CH₃BF₂ and CD₃BF₂,¹⁷ and is shown in Fig. 5. The sharp doublet at 480.4 and 482.0 cm⁻¹ was again caused by the BF₃ impurity. Finally, the BF₂ in-plane rock, $\nu_{14}(a_1'')$, was assigned to a doublet type-B band centered at 307 cm⁻¹, and is shown in Fig. 6. The observed P-R separation of approximately 10 cm⁻¹ was in good agreement with the calculated value of 8.4 cm⁻¹.

Skeletal Vibrations

The seven remaining normal modes of vibration of $CH_3C \equiv CBF_2$ were all associated with the linear skeletal chain of the molecule. The C=C stretch, $\nu_2(a_1')$, was easily assigned to an intense infrared band at 2228 cm⁻¹. A set of barely resolved but reproducible transitions at 2231.3, 2233.8, and 2235.0 cm⁻¹ were probably caused by hot bands, as this is a common feature of $C \equiv C$ stretches in other molecules. A less intense type-A absorption characterized by a weak Q branch at 1018.5 cm⁻¹ was taken to be the C-C stretching mode, $\nu_5(a_1')$. The assignment of the C-B stretch, $\nu_6(a_1')$, proved to be more difficult since it was expected that this mode would absorb as an isotopically split type A-band around 750 cm⁻¹. Only two rather weak absorptions were observed in this region, at 747 and 782 cm^{-1} . The ν_6 mode was tentatively assigned to the 782-cm⁻¹ absorption based on supporting evidence from a lowtemperature thin-film spectrum of this region which showed a doublet at 770 cm⁻¹, suggestive of isotopic splitting.

The assignment of the two doubly degenerate skeletal bending vibrations to absorptions in the 500-250-cm⁻¹ region was based solely on group frequencies. The C-C=C bend, $\nu_{12}(e')$, was assigned to a weak infrared band at 371 cm⁻¹ which is consistent with spectra of other molecules of the form CH₃C=CX (X=H, Cl, Br, I). The C=C-B bend, $\nu_{11}(e')$, was assigned to a somewhat stronger, structureless absorption at 406 cm⁻¹.

Table II summarizes the vibrational assignment of the normal modes for $CH_3C \equiv CBF_2$.

THERMODYNAMIC PROPERTIES

Although experimental values for the rotational constants of $CH_3C\equiv CBF_2$ were not available and only approximate values for the gas phase frequencies of the ν_3 , ν_9 , and ν_{10} normal modes were known, it was decided that the calculation of the thermodynamic properties of this molecule would none the less prove useful.

These quantities were calculated from the observed vibrational wavenumbers of Table II and the previously given estimates for the rotational constants on the basis of an ideal gas in its standard state and a rigid-rotor harmonic-oscillator approximation. A contribution for free internal rotation was included in the total partition function using an internal symmetry number of 6. The results are shown in Table III.

* Based in part on the Ph.D. dissertation of P. R. Reed, Jr., submitted to the Graduate School, Lehigh University, 1970. Presented at the 25th Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Sept., 1970.

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Reactions in Crystalline Lattices: Spectroscopic Evidence for the Oxidation of Sm^{2+} to Sm^{3+} in KCl*

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With varying concentrations of O2 and H2O, oxidation of Sm2+ to Sm3+ is observed. Experimental proof of the oxidation process is given by: (1) the disappearance of the characteristic absorption bands of Sm^{2+} , accompanied by a dramatic decrease in the $Sm^{2+5}D_0 \rightarrow^7 F_J$ fluorescence intensity; (2) the observation of the ${}^{6}H_{5/2} \rightarrow {}^{4}I_{13/2}$ absorption lines of Sm³⁺; and (3) the reappearance of Sm²⁺ fluorescence lines upon gamma irradiation of the oxidized sample. The discovery of a cubic Sm^{2+} site, which gives rise to a ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ fluorescence transition with a magnetic splitting factor of 1.48 ± 0.05 in excellent agreement with the Landé g_{λ} factor of 1.5, is also reported. The significance of the hitherto unobserved cubic site is discussed.

I. INTRODUCTION

When divalent impurity cations enter into an alkali halide lattice, a corresponding number of cation vacancies are formed in order to maintain electroneutrality.¹ These aliovalent cation-vacancy pairs exist in a distribution of various sites with the relative population numbers governed by Maxwell-Boltzmann statistics.²⁻⁴ In the present work, we explore the possible interactions of the Sm²⁺-K⁺ vacancy pairs in KCl with O₂ and H₂O molecules in an annealing atmosphere at elevated temperatures. In particular, we seek the answers to the questions: (1) Can Sm³⁺ exist in the KCl lattice? (2) Can an Sm^{2+} ion occupy a cubic site in KCl without a nearby charge compensation?

The annealing experiments have been performed under atmospheres with controlled amounts of contaminants such as H₂O and O₂. The central result is the controlled oxidation of Sm²⁺ to Sm³⁺ in KCl. Although the reduction of rare-earth ions in single crystals to lower oxidation states is well known,^{5,6} the

oxidation of a rare-earth ion to a higher oxidation state in a host lattice has hitherto not been reported. The present result is somewhat unexpected in view of the fact that an Sm³⁺ ion would require two chargecompensation defects in KCl. The incorporation of trivalent cations in alkali halides has thus far been considered to be energetically unfavorable. The ability to control the valence of the rare-earth ion in crystalline hosts is of great practical importance. The reduction of trivalent rare-earth ions to the divalent state was motivated by the fact that the divalent rare-earth systems are good laser materials.⁷ In the present case, the oxidation of Sm²⁺ to the trivalent state is motivated by the fact that KCl: Sm³⁺: Eu³⁺ could be an important material in achieving highly efficient $10-\mu$ quantum counter up-conversion.8,9

The proof for the existence of Sm³⁺ ions has been given by means of three sets of experiments. First, the absorption bands of the Sm²⁺ ions in samples annealed under a controlled atmosphere containing H₂O and O₂ have practically disappeared. The intensities of all the