Table I. Depolarization cross sections and mean reorientation angles averaged over all rotational states for I_2^*–M collisions.

| M | σ_{pol}^2 (cm$^2 \times 10^{16}$) | | | | |
	$\Delta v' = 0$ (all J')	$\Delta v' = 0$ ($\Delta J' \neq 0$)	$\Delta v' = +1$	$\Delta v' = -1$	$\langle \frac{2}{3} \sin^2 \alpha \rangle_{J'}$
H_2	2.9	5.3	...	...	0.70
He	3.7	7.0	12.9	9.4	0.74
Ne	22.7	22.8	...	...	0.88

observed depolarizations are greater for $\Delta v' \neq 0$ than for $\Delta v' = 0$, it is also true that there is greater rotational energy transfer accompanying vibrationally inelastic collisions. Using the known[5] $\Delta J'$ distributions for $\Delta v' = \pm 1$ collisions, and the $(\Delta J' \neq 0)$ depolarization cross section already found, we can calculate an effective $\sigma_{pol}^2 = (9-10) \times 10^{-16}$ cm^2 for $\Delta v' = \pm 1$. Thus, it appears that the observed depolarization may arise solely from the change in rotational state, and not reflect any significantly greater degree of reorientation of the molecular angular momentum accompanying the presumably "stronger" vibrationally inelastic collisions.

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Force Constants of the Metaborate Ion in Alkali Halides*

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Previous infrared studies[1] of the metaborate ion as a substitutional impurity in alkali halide lattices have yielded generally concordant values for the bending and antisymmetric stretching fundamental frequencies as well as the strongest combination mode which is the Fermi doublet $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$. Isotopic species reported include $^{10}B^{16}O_2^-$, $^{11}B^{16}O_2^-$.

The cyanate ion[2] in similar hosts exhibits a splitting of the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ doublet which is almost identical with the splitting of ν_1 and $2\nu_2$ which are observable for the unsymmetric linear triatomic molecule, but forbidden in the infrared spectrum of metaborate. In cyanate, the sums of the observed values of ν_3 and of either of the observed values of the ν_1, $2\nu_2$ doublet are about 20 cm^{-1} greater than the respective members of the $\nu_1 + \nu_3$, $2\nu_2 + \nu_3$ doublet. By transferring this anharmonicity correction from cyanate to metaborate we can predict the positions of the infrared inactive ν_1,

$2\nu_2$ frequencies as follows (KBr host):

(i) $^{10}B^{16}O_2^-$:

$$(2\nu_2 + \nu_3) - \nu_3 + 20 = 3251 - 2029 + 20 = 1242 \text{ cm}^{-1},$$
$$(\nu_1 + \nu_3) - \nu_3 + 20 = 3095 - 2029 + 20 = 1086 \text{ cm}^{-1},$$

(ii) $^{11}B^{16}O_2^-$:

$$(2\nu_2 + \nu_3) - \nu_3 + 20 = 3145 - 1958 + 20 = 1207 \text{ cm}^{-1},$$
$$(\nu_1 + \nu_3) - \nu_3 + 20 = 3022 - 1958 + 20 = 1084 \text{ cm}^{-1}.$$

With the search area for these previously unknown energy levels rather narrowly circumscribed, we proceeded to examine the ν_2 region of the spectrum of single crystals of KBr and KCl doped with metaborate in order to find the difference frequencies (hot bands) for the transitions $01'0 \rightarrow 10°0$ and $01'0 \rightarrow 02°0$ which

TABLE I. New transitions and energy levels of metaborate ion in alkali halide hosts ($T=305°K$).

Initial state	Final state	KBr		KCl	
		$^{11}BO_2^-$	$^{10}BO_2^-$	$^{11}BO_2^-$	$^{10}BO_2^-$
00°0	02°1	3145	3251	3163	
00°0	10°1	3023	3095	3042	
00°0	01'0	588.6	609.5	589.5	
01'0	02°0	613.5	631.5	617	
01'0	10°0	490	474	495	
00°0	02°0	(1202.1) 1203ᵃ	(1241)	(1206.5)	1244ᵃ
00°0	10°0	(1078.6) 1079ᵃ	(1083.5)	(1084.5)	1090ᵃ
ν_1 (unperturbed)		1103.5	1105.5	1112	1112

ᵃ All frequencies are observed in the infrared spectrum except these marked "ᵃ", which were observed in the Raman effect, and those enclosed in parentheses, which were calculated using the Ritz principle.

are infrared allowed and have been detected in cyanate studies.[2] The results are summarized in Table I which includes some previously unreported data on the combination bands and which gives also the calculated positions of ν_1 and $2\nu_2$ which, since they are obtained by the Ritz principle, involve no assumptions about anharmonicity; it is seen that the results found are in good agreement with the prediction based upon the transferred anharmonicity correction.

Subsequent to the infrared studies which have just been described, we were able to observe several of the crystal samples with Laser excited Raman techniques. The lines found in this way are also reported in Table I. The intensity ratio for this Fermi doublet is approximately 2.5 to 1 for $^{11}BO_2^-$ and 3.3 to 1 for $^{10}BO_2^-$, the

lower frequency in each case being stronger. By neglecting the effects of anharmonicity except via the Fermi resonance, we have estimated the unperturbed value of ν_1 as shown in the last line of the table. Since sufficient levels of metaborate are not yet known to correct for anharmonicity, we have calculated the force constants using the observed values of ν_1 given in the table together with previously reported[1] values for ν_3. The BO stretching constant turns out to be $f_{BO} = 11.4$ mdyn/Å and the interaction constant is $f' = 2.2$ mdyn/Å (KBr host). Similar calculation of the force constants of the isoelectronic molecules CO_2 and NO_2^{+} [3] yields for $f_{CO} = 15.5$ and $d_{NO} = 17.3$ mdyn/Å. Although the spectroscopic measurements come from different phases for the isoelectronic sequence BO_2^-, CO_2, NO_2^+, the trend of increasing bond strength with increasing nuclear charge of the central atom is clear. It may also be of interest to note that the value of $\nu_1 = 1104.5$ (KBr average) is found to be larger than $\nu_1 = 1070$[4] in the neutral BO_2, just as $\nu_1 = 1335$ (average of Fermi doublet) in CO_2 is greater than $\nu_1 = 1280$ in CO_2^+.[5]

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Raman Spectroscopy, Rotational Isomerism, and the "Rotator" Phase Transition in n-Alkanes

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Many n-alkanes exhibit a first-order solid–solid phase transition a few degrees below their melting points. The earliest molecular interpretation of this phenomenon was given by Muller[1] and later studies[2] have tended to reinforce his view that the phase transition is associated with the onset of hindered rotation

of the extended alkane chains about their long axes. Recently Pechold and his co-workers[3–6] have proposed a "kinkblock" model in which the phase transition is associated with the occurrence of rotational isomers belonging to a particular class, the so-called kink-isomers. Since the n-alkanes and their polar derivatives