than does the lanthanum compound even though the cation size is greater, it is apparent that the electronic and mass effects are significant and the spectral differences are therefore to be expected. A more detailed discussion of the crystallography of these compounds is to be found in the paper by Sawyer, *et al.*[6]

It may be noted that the usual effects of the lanthanide contraction are carried over to the spectra of these compounds. For the type II compound the increase in frequency of a mode with increasing atomic number (decreasing cation radius) does occur regularly for all four modes.

Acknowledgment.—We are grateful to Miss K. Reimer for taking the infrared spectra and to the United States Atomic Energy Commission for financial support.

Contribution from the Department of Chemistry,
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Infrared Spectra of Bicarbonate Ions Formed in Solid Alkali Halides by Oxyanion Oxidation

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When heated, pressed disks of several alkali halides react with substances such as potassium permanganate in the presence of water and carbon dioxide to yield bicarbonate ions occupying anion sites in the host alkali halides. This method has been used to disperse the bicarbonate ion in nine alkali halides for use in studies of the effect of environment on vibrational spectra. In favorable cases, infrared spectra have been obtained virtually free of interfering absorption due to such substances as potassium carbonate, and as a consequence erroneous vibrational assignments made by earlier investigators have been corrected. The ease of formation of carbonaceous species has been related to properties of the host alkali halides, and it is shown that the carbon and hydrogen in the carbonaceous species come mostly from atmospheric water and carbon dioxide.

Introduction

We have discovered in a study of the infrared spectra of the chlorate ion dispersed in various alkali halides[2] that this ion, and other oxidizing oxyanions, in the presence of traces of water and carbon dioxide, will react in solid alkali halide disks to yield monomer bicarbonate ion when the disks are heated. The presence of the bicarbonate ion was deduced from the excellent agreement of our results for the wave number of the strong bands of HCO_3^- in KCl, KBr, and KI with those obtained for the same systems by Bernitt, *et al.*[3] (hereafter referred to as BHH). We have obtained HCO_3^- spectra virtually free of absorption bands due to species closely related to monomer bicarbonate such as K_2CO_3, and dispersed CO_3^{2-}, whereas BHH, who used bicarbonate salts as a source of monomer bicarbonate, obtained spectra obscured by strong absorption due to such unwanted species. This has enabled us to correct some misassignments made by BHH, and, with our technique of *in situ* generation of monomer HCO_3^-, we have increased the number of host environments from the three reported by BHH to the nine indicated in Table I.

Table I

Yields and Products Formed by Heating an Oxidizing Agent in Alkali Halide Disks[a]

	Alkali halide								
	KCl	KBr	KI	RbCl	RbBr	RbI	CsCl	CsBr	CsI
$KMnO_4$	As Bl Cm El	Am Bm Cm Dm Em	Al Bm Cm Em	As Bl Cm El	Am Bm Cm Dm Em	As Bl Cm El	As Bl Cm El	As Bl Cm Dl El	Al Bm Cm Em
$KClO_3$	0	0	Al Cs Dl	0	0	0	0	As	Al Dl
$KHCO_3$	As Bl Fm	As Bl Fm	As Bl Fm	. . .	. . .	. . .	. . .	. . .	. . .

[a] Notation: Capital letters denote product species: A = HCO_3^-, B = M_2CO_3 (M = K, Rb, or Cs), C = CO_3^{2-}, D = XO_3^- or MXO_3 (X = Br or I), E = MnO_2, F = HCO_2^-. Small letters denote relative yield: s = small; m = medium; l = large. 0 denotes that no reaction was detected. . . . denotes that the system was not investigated.

Experimental Section

Chemicals.—Merck "Suprapur" and reagent grade alkali halides were used. These Analar grade chemicals were used without further purification: $KClO_3$, $KHCO_3$, KIO_3, $KMnO_4$, $K_2Cr_2O_7$, MnO_2, HCO_2K, and BaO_2.

Sample Preparation.—Mixtures of the oxidizing salt (or potassium bicarbonate) and the alkali halide were mixed with an agate pestle and mortar or by flash evaporation. Usually the mixtures were ground for 10 min while exposed to the lab-

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(1) To whom correspondence regarding this paper should be addressed.

(2) P. M. Maguire and H. E. Rubalcava, unpublished investigations.

(3) D. L. Bernitt, K. O. Hartman, and I. C. Hisatsune, *J. Chem. Phys.*, **42**, 3553 (1965).

oratory air. The mixtures were compressed into 500-mg disks of 15-mm diameter in a standard evacuable die at *ca.* 90 tons in.$^{-2}$ pressure.

Flash Evaporation.—A mixture of 500 mg of alkali halide and 0.5 mg of added salt was heated in the minimum volume of water to give a saturated solution at its boiling point. When the solution began to boil, it was dashed into a well in a massive aluminum block which had been heated to 180–200°. Evaporation was completed in less than 1 sec. The dried mixture was then finely ground and made into a disk.

Disk Heating.—Disks were heated by three methods. (i) The disk was placed under an infrared lamp (Osram, 250 W) and enclosed with aluminum foil to prevent drafts. Disk temperatures of 350–380° were obtained by raising or lowering the lamp; the temperature was measured with a thermocouple embedded in a test disk. (ii) Disks were heated in an evacuable heating cell at 350–450° by a grid of nichrome tape. (iii) Higher temperatures were obtained by securely wrapping a disk containing potassium bicarbonate and a thermocouple in aluminum foil and heating them in a bunsen flame at 500°.

Standard Procedure.—The relative ease of formation and trapping of bicarbonate monomer in the various alkali halides was established by the following standard procedure. Potassium permanganate (0.5 mg) and 500 mg of alkali halide were mixed manually and compressed into a disk which was heated for 15 min by method (i) at 350–380°, and the disk was cooled over silica gel. Heating changed the disk color to brown-gray, made it opaque, and caused tiny cracks and blisters. Transparency was restored by recompressing the disk at a pressure of 90 tons in.$^{-2}$ for 5 min.

The concentration of potassium permanganate and the dryness of the disk were varied systematically to obtain a high yield of dispersed HCO_3^- and a small amount of unwanted products. For 500 mg of KBr satisfactory results were obtained with 0.5 mg of $KMnO_4$ and by drying the disk for 20 min at 100° *in vacuo*.

Spectra.—Spectra were obtained with a Grubb-Parsons "Spectromaster" using slit program 10. Spectra at *ca.* 125°K were obtained in a conventional cell cooled with liquid nitrogen. Bands near 600 cm^{-1} were measured to an accuracy better than ±1 cm^{-1} by using the bands of chlorate ion present in the disks. These bands have been measured with reference to standard ammonia and water absorptions[4] in this laboratory[2] and elsewhere;[5] the two independent sets of measurements agreed to better than 0.5 cm^{-1}.

Results and Discussion

Chemical Section.—This study of aspects of the chemistry and spectra of the monomer bicarbonate ion involved the examination of several systems, each composed of disks of a given alkali halide containing a particular oxidizing agent. The systems given in Table I were studied fairly extensively.[6]

As shown in Figure 1 the infrared spectrum of a KI disk containing dispersed ClO_3^- changes after it has been heated at *ca.* 350° for 30 min. Bands due to ClO_3^- [2,5] disappear and new bands appear. If the disk is subsequently crushed, finely ground, and recompressed into a new disk, some bands persist, but others do not as shown in spectrum C. The bands near 800 cm^{-1} are assigned to KIO_3 because they appear if KIO_3 is dispersed in KI by the usual "KBr pellet" technique, and the sharp band near 2150 cm^{-1} is due to cyanate ion.[3,7] The sharp bands of spectrum B in Figure 1 which do not appear in spectrum C are assigned to HCO_3^- dispersed in KI because of the excellent agreement, except as discussed below, with the results of BHH (see Table III).

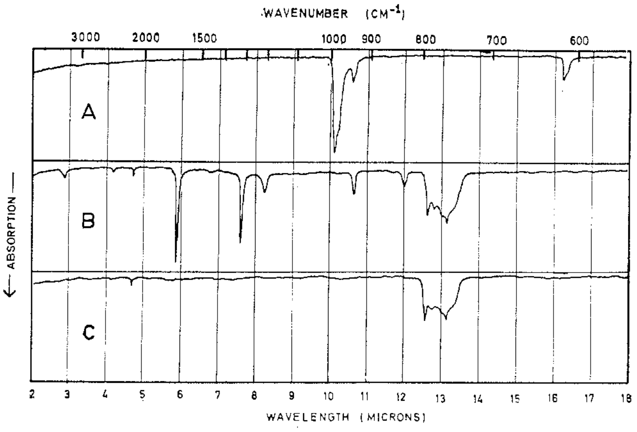

Figure 1.—(A) spectrum of KI disk containing dispersed ClO_3^-; (B) spectrum of HCO_3^- after heating disk A for 15 min at 350–380°; absorption due to trapped CO_2, NCO^-, and KIO_3 is also evident; (C) spectrum after regrinding disk B; absorption due to NCO^- and KIO_3 remains. All spectra were recorded at room temperature.

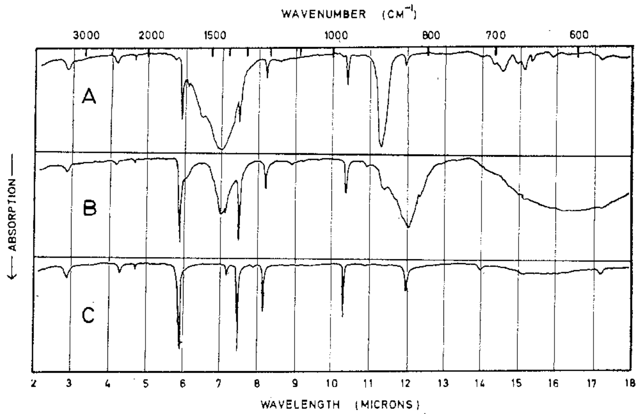

Figure 2.—Spectra at *ca.* 125°K of HCO_3^- in KBr, prepared as indicated: (A) by heating $KHCO_3$; (B) by heating $KMnO_4$ under standard conditions; (C) by heating $KMnO_4$ under optimum conditions.

Chlorate ion will generate HCO_3^- easily in both KI and CsI, but not in other alkali halides. However, $KMnO_4$ will easily generate the ion in other host salts. Figure 2 shows spectra of HCO_3^- in KBr obtained from potassium bicarbonate, from potassium permanganate oxidation with an excess of the oxidant, and from potassium permanganate oxidation under favorable conditions for HCO_3^- formation. Spectrum 2A agrees substantially with that of the same system given in ref 3. The characteristic sharp bands of the dispersed bicarbonate ion appear in all three spectra, but it is clear from the relative simplicity of spectrum

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(4) "IUPAC Tables of Wavenumbers," Butterworth and Co. Ltd., London, 1961.

(5) G. N. Krynauw and C. J. H. Schutte, *Spectrochim. Acta*, **21**, 1947 (1965).

(6) Other systems were examined only once or twice in exploratory experiments. Monomer bicarbonate formed with KIO_3, K_2CO_3, MnO_2, HCO_2K, and BaO_2; it did not form with $NaAuCl_4$, H_2PtCl_6, $KClO_4$, or $K_2Cr_2O_7$. Potassium iodide was the disk material in these experiments.

(7) A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959).

2C that extra bands are present in spectrum 2A. These are due mostly to undispersed potassium carbonate, dispersed carbonate ion, and trapped carbon dioxide (these species will frequently be referred to as carbonate-like species). The broad absorption near 600 cm^{-1} is due to MnO_2. Figure 2B shows clearly the typical result that an excess of the oxidizing agent gives undispersed potassium carbonate. Spectrum 2C illustrates the degree of success achieved in minimizing unwanted absorption due to carbonate-like species.

Bicarbonate ion yield was not equal in all host crystals when a given oxidizing agent was used, nor was it equal in a given host with different oxidizing agents. For example, chlorate ion yielded HCO_3^- easily in KI and CsI, but not in any other host. Potassium permanganate gave large yields of HCO_3^- and of related species in KI and CsI, a good yield in KBr, moderate yields in RbBr and KCl, but relatively poor yields in RbI, CsBr, CsCl, and RbCl. These experiments, as described above, were made under standard conditions of reagent composition, pyrolysis time and temperature, and disk preparation procedure. These results were sufficiently reproducible to suggest a qualitative relative reactivity order for the various alkali halides: $KI \cong CsI > KBr > RbBr > KCl > RbI > CsBr \cong CsCl \cong RbCl$.

Rubidium iodide differs from KI and CsI because chlorate ion did not generate HCO_3^- in it, and the yield with $KMnO_4$ was low under conditions which gave good yields in the other two iodides. This stability of RbI, which is discussed below, was also evident in the process of dispersing $KMnO_4$ and preparing the disk: CsI and KI both showed the reddish color of oxidation products of the host iodide, but RbI did not; it showed only the purple color of dispersed $KMnO_4$.

In situ generation of HCO_3^- requires an oxidizing agent, water, and carbon dioxide. Neither HCO_3^- nor carbonate-like species formed unless an oxidizing agent had been added to the alkali halide disk. This was shown by simultaneously heating doped disks and undoped disks: HCO_3^- appeared only in the doped disk and never in the undoped disk. The experiments in which oxyanion-doped disks were dried under vacuum at 100° indicated the participation of water and carbon dioxide. Both dried and undried disks made from the same batch of KI doped with $KMnO_4$ were heated together. In every case the undried disks gave copious yields of carbonate-like species, but the disks dried under vacuum for 1 hr showed no absorption due to such species. These results show, if it is accepted that water and carbon dioxide will escape from alkali halide disks, that the sources of carbon and hydrogen were atmospheric water and carbon dioxide.

Van der Maas and Tolk[8] discussed the permeability of KBr disks to water. Investigations in this laboratory[9] have shown that water and formic acid will escape from alkali halide disks made by flash evaporation from aqueous formic acid. The undried disks showed a complex spectrum, largely of water and formic acid, but the dried disks showed only the spectrum of dispersed formate ion. Iodide disks were dried most easily, bromide disks were more difficult to dry, and chloride disks were the most difficult to to dry. These results suggest that the iodides are most permeable and the chlorides are least permeable and show that water and formic acid will escape from the disks. Thus vacuum drying should remove CO_2 from compressed alkali halide disks.

A priori, atmospheric water and carbon dioxide need not be the only sources of carbon and hydrogen: ubiquitous airborne particles of organic matter, *e.g.*, microorganisms and dust, could also supply these elements. However, if these were an important source, vacuum drying would not prevent the formation of the carbonate-like species because the relatively large particles would not be removed by the process. Subsequent oxidation, during pyrolysis, of trapped organic matter would give carbon dioxide and water and, eventually, bicarbonate ion and related species; but that does not happen; hence, large particles of organic matter are not an important source of carbon and hydrogen. On the other hand, the bands appear to the same degree in a given salt with a given oxidizing agent regardless of the purity, whether "Suprapur" or reagent grade, of the alkali halide, suggesting that the carbon and hydrogen come from the air during the disk preparation. Clearly, adsorption of water and carbon dioxide is a most reasonable process for introduction of carbon and hydrogen.

We believe that the HCO_3^- and carbonate-like species are formed because the carbon dioxide–water mixture donates protons in the oxidation of the host halide ions. For example, as in the possible initial reactions

$$H_2CO_3 + ClO_3^- + 2I^- \longrightarrow I_2^- + ClO_2 + OH^- + HCO_3^-$$

and/or

$$H_2O + ClO_3^- + 2I^- \longrightarrow I_2^- + ClO_2 + 2OH^-$$

Both steps would be followed by

$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$$

The chlorine dioxide (or other reduced chlorine compound) would then decompose to yield, eventually, chloride ion. Any molecular oxygen formed would escape from the porous disk. Similar reactions are proposed for other oxidizing agents and alkali halides. Although hydroxide ion appears in the proposed mechanism, we have no spectroscopic evidence for it. This is reasonable because at the pyrolysis temperatures the smaller water molecules should escape more quickly than the larger carbon dioxide molecules, and residual carbon dioxide would tend to neutralize any hydroxide ion formed.

The observed order of ease of formation of dispersed bicarbonate ion or carbonate-like species in different alkali halides with a given oxidizing agent is not un-

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(8) J. H. Van der Maas and A. Tolk, *Spectrochim. Acta*, **18**, 235 (1962).
(9) H. E. Rubalcava, unpublished investigations.

expected. Consider two alkali halides: the yield of HCO_3^- would be favored by a lower melting point, by a lower heat of formation, by a larger volume of the anion site, and by a less stable anion (smaller electron affinity). Thus, the yield of such species should be highest in the iodides, intermediate in the bromides, and lowest in the chlorides. This is, roughly, the order observed except for rubidium iodide which, as mentioned above, behaves anomalously. Our experience that it is easier to disperse small ions, such as chlorate or formate, in the iodide than in the bromide of a given alkali metal,[2,9] together with repeated failures to achieve a better dispersion of HCO_3^- in RbI than in RbBr, convinces us that the primary cause for the stability of RbI is not related to the size of the anion vacancy, but must be kinetic. During pyrolysis, diffusion of mobile species and the redox reactions of the halide ions and the oxidizing agents are, in effect, competing reactions because, if the redox processes are too slow, the carbon dioxide and water escape before appreciable amounts of carbonaceous species are made. This has been shown by the vacuum-drying experiments. Among factors which probably affect the rate of the redox step is the initial distance between halide ions if they combine as in the suggested mechanism; if this distance is sufficiently large, the redox step may be slowed considerably. Therefore, it is possible that RbI is anomalous because the separation of nearest neighbor anions is greater in it than in any other of the alkali halides studied.

We assume, as do BHH, that the bicarbonate ion is at anion sites. The sharpness of its absorption bands, the host dependence of their wave number, and the lack of satellite bands due to ions in different types of sites all suggest anion substitution. Various mechanisms may explain this. If water droplets are present in the disk, anionic substitution may occur when solid precipitates as water escapes during pyrolysis. This would explain the formation of K_2CO_3 with an excess of oxidant: the resulting quantity of carbonaceous product would exceed the amount soluble in either the water or the host, and it would precipitate as undispersed product. Another possible mechanism involves the occurrence of local "hot spots" due to the sudden release of heat in the redox reaction; should the temperature be high enough, the host would melt, the bicarbonate ion would dissolve in the molten salt, and on cooling it would be trapped in the resolidified host. Dispersion may also occur when the pyrolyzed disk is recompressed to regain its optical transparency. It is widely accepted[7,10] that small ions enter anion sites when disks are compressed.

Spectroscopic Section.—We assume that the ion HCO_3^- is planar with two of the CO bonds dynamically equivalent. Table II describes the seven in-plane and two out-of-plane normal modes of vibration of the ion.

TABLE II

HCO_3^- NORMAL MODES OF VIBRATION[a]

ν_1	O–H str	ν_6	CO_2 bend
ν_2	CO_2 asym str	ν_7	(HO)–CO_2 in-plane bend
ν_3	CO_2 sym str		
ν_4	H–O–C bend	ν_8	(HO)–CO_2 out-of-plane bend
ν_5	(HO)–C str		
		ν_9	H–OCO_2 torsion

[a] The descriptions of the normal modes are approximate.

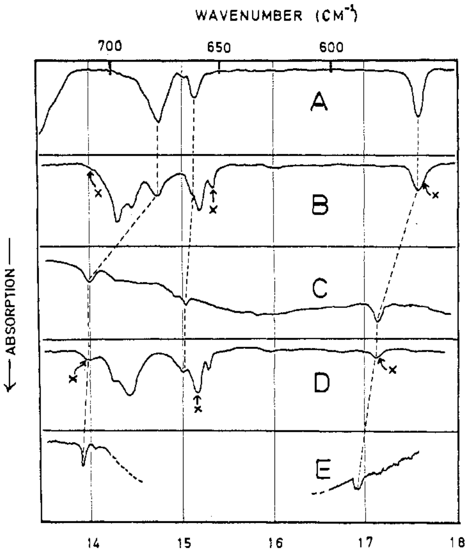

Figure 3.—Details of HCO_3^- spectra in the potassium halides in the region 550–750 cm^{-1}. All spectra were run at *ca.* 125°K. Disks were prepared as indicated: (A) KI (*in situ* with $KClO_3$); (B) KI (from $KHCO_3$); (C) KBr (*in situ* with $KMnO_4$); (D) KBr (from $KHCO_3$); (E) KCl (*in situ* with $KMnO_4$). HCO_3^- absorption in (A), (C), and (E) not observed at room temperature. × indicates the position where BHH report absorption due to HCO_3^-.

Although we agree closely with BHH on most of the vibrational assignments of HCO_3^- in the three potassium halide hosts, we differ, as indicated in Table III, from them on the assignments of ν_6, ν_7, and ν_9. The differences probably arise because of uncertainty caused by spurious bands due to impurities formed when potassium bicarbonate is heated in the BHH method. Spectrum A of Figure 2 is that of a sample prepared by heating a KBr disk containing $KHCO_3$; it reproduces fairly well the spectrum of the same system as shown in Figure 1 of ref 3.[11] It also shows broad bands near 1400 and 900 cm^{-1} ascribable to crystallites of undispersed potassium carbonate.[12] By contrast, spectrum C of Figure 2, which is of *in situ* generated HCO_3^- in KBr, shows clearly the strong, sharp bands of dispersed HCO_3^-, and no trace of absorption due to K_2CO_3 appears. The weak, sharp band near 1400 cm^{-1} is very likely due to dispersed CO_3^{2-}.[13] No absorption due to potassium permanganate remains,

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(10) J. I. Bryant and G. C. Turrell, *J. Chem. Phys.*, **37**, 1069 (1962).

(11) The spectrum published by BHH indicates a somewhat better dispersion of the bicarbonate ion than that achieved in the disk yielding spectrum 2A, but not as good a that in the disk of spectrum 2B.

(12) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(13) H. W. Morgan and P. A. Staats, *J. Appl. Phys.*, **33**, 364 (1962).

TABLE III

WAVE NUMBERS OF THE FUNDAMENTALS OF THE BICARBONATE ION DISPERSED IN ALKALI HALIDES[a]

	Host								
	KCl	KBr	KI	RbCl	RbBr	RbI	CsCl	CsBr	CsI
ν_1	3340 (1)	3390 (0)	3418 (1)	3344	3401	3413		3330	3333
ν_2	1702 (1)	1696 (1)	1687 (0)	1675	1691	1689	1687	1684	1678
ν_3	1346 (0)	1338 (0)	1327 (−1)	1339	1329	1320	1343	1330	1315
ν_4	1218 (0)	1211 (0)	1205 (0)	1252	1214	1200	1239		1225
ν_5	971 (0)	961 (1)	949 (0)	976	957	950	979	948	943
ν_6	720[b] (7)	715[b] (3)	678[b] (−36)		711				709
ν_7	591[b] (2)	581[b] (2)	571[b] (5)						582
ν_8	840 (0)	838[b] (3)	835 (0)			835			828
ν_9	c	667[b] (7)	662[b] (7)						

[a] Numbers in parentheses are the wave numbers reported in this study minus those reported by BHH. Blanks mean that we have not observed the corresponding band. [b] These wave numbers differ from those reported by BHH by more than amount attributable to precision. See text. [c] BHH give 672 cm^{-1}.

and the reaction product manganese dioxide only gives the weak, broad band centered near 600 cm^{-1}. Spectra C and D of Figure 3 show, in detail, for HCO_3^- in KBr the spectral differences in the controversial region between 800 and 550 cm^{-1}. The spectrum of the *in situ* generated species, spectrum C, has only the three weak bands at 715, 667, and 581 cm^{-1}, whereas the spectrum of the disk prepared by the BHH method, spectrum D, shows these and several other stronger bands. These extra bands cannot be assigned to HCO_3^- because they do not appear in the spectra of disks which, if the assignments above 900 cm^{-1} are accepted, have much of the dispersed bicarbonate ion and little of the unwanted carbonate-like species. Although the precise assignments made by BHH are incorrect, the reasons given by them for the approximate positions of the low-wave-number bands are convincing and lead to the assignments given in Table III for the three weak bands of the *in situ* generated HCO_3^-.

The analysis of the spectrum of HCO_3^- dispersed in KI is similar to that for KBr. Spectrum B of Figure 1 shows the spectrum of HCO_3^- isolated in KI by *in situ* generation with potassium chlorate. Our assignment of the strong, sharp bands of this spectrum agree with those made by BHH for a disk prepared by heating potassium bicarbonate dispersed in KI. Spectrum A of Figure 3 shows the region of ν_6, ν_9, and ν_7 for a KI disk which, as in Figure 1B, shows no absorption due either to K_2CO_3 or CO_3^{2-} near 1400 cm^{-1}; B of Figure 3 is the corresponding spectrum of a KI disk prepared by the BHH method. Both disks absorb at 678, 662, and 571 cm^{-1}, but the disk made by the BHH method has several extra bands. The argument used above for the KBr case applies to KI as well, and the three bands common to both disks are assigned to ν_6, ν_9, and ν_7, respectively.

The situation for HCO_3^- spectra obtained in a KCl host is essentially like that for KI, or for KBr, except that the difficulty of dispersing HCO_3^- in KCl makes the spectra poorer than in KI or KBr. The quality of our best spectrum in KCl is slightly poorer than that of spectrum B of Figure 1. As before, our assignments for the strong, sharp bands agree with the assignments made by BHH, but we disagree for the low-wave-number region. We assign the two stronger bands in spectrum E of Figure 3 to ν_6 and to ν_7 of the dispersed ion. Presumably ν_9 absorbs too weakly to be observed in the region, indicated by a dashed curve, where decomposition products of $KMnO_4$ interfere. The stronger band at 720 cm^{-1}, rather than the very weak band at 713 cm^{-1}, is assigned to ν_6 because this gives a monotonic relation between the frequency of this mode and the size of the anion site in the host crystal. This assignment also conforms with those for KBr and KI in that the relative maximum intensities of ν_7 and ν_9 are approximately equal in a given host crystal.

In Figure 3 we indicate several discrepancies between our results and those reported by BHH. For example, they report a band in KI at 714 cm^{-1}, which we do not observe; the nearest band is at 701 cm^{-1}. We are unable to offer a positive reason for the discrepancies; our spectra were calibrated as described in the Experimental Section, and the results given for the spectra in question are the average of at least five measurements with standard deviations smaller than the differences.

Since gaseous carbon dioxide absorbs at 667 cm^{-1}, the possibility arises that bands near there may be due to CO_2 trapped in the disk. Ideally, intensity correlations with the obvious CO_2 absorption near 2350 cm^{-1} would largely remove uncertainty as to whether the low-wave-number band is due to CO_2. Unfortunately, all of the bands possibly due to CO_2 absorb too weakly to permit a definite conclusion. However, we suggest tentatively that ν_2 of trapped CO_2 causes the complex band centered at 661 cm^{-1} in the KI and KBr spectra (Figures 3B and 3D).

The quality of the spectra of HCO_3^- dispersed in the rubidium and cesium halides differs markedly: that in CsI is very good, that in RbBr is moderately good, but those in RbI, RbCl, CsBr, and CsCl are poor, and it is necessary to study the spectra obtained at *ca.* 125°K to find the HCO_3^- bands. The results are given in Table III; all of the bands were observed in the spectra of at least two disks.

The frequency shifts of the fundamentals of HCO_3^- dispersed in alkali halides are like those of most ions that have been studied dispersed as single ions occupying single substitutional sites in alkali halide hosts;[2,5,7,9,10,14] *i.e.*, for a given fundamental, ν_i, the frequencies in nearly all cases decrease in the order ν_i(MCl) > ν_i(MBr) > ν_i(MI).[15] However, ν_1 is remarkable because, atypically, it shows a pronounced variation in the opposite direction; *e.g.*, ν_1(KCl) lies 78 cm^{-1} *below* ν_1(KI). Similar behavior is observed for all of the ν_1 bands that we have observed. We know of no other case in which a host dependence similar in magnitude to that of ν_1 has been observed. Maki and Decius[7] calculated the shift in ν_3 of cyanate ion due to dipole–induced dipole interactions in several alkali halides and found a small reverse trend, but the calculated shift is only about one-tenth of that observed for the bicarbonate ion. It can be argued that effects such as hydrogen bonding and dependence of the C–O–H angle on the substitutional site geometry would cause ν_1 to vary in the observed direction. However, a satisfactory explanation of this unusual behavior requires more experimental evidence than is now available.

Although we find attractive the assignments of BHH for the fundamentals of $HC^{12}O_3^-$, we do not find entirely convincing the additional vibrational assignments for the labeled isotopic species $HC^{13}O_3^-$, $DC^{12}O_3^-$, and $DC^{13}O_3^-$, all dispersed in KBr. Some of the proposed assignments show, in our opinion, an implausible mass independence. For example, in $HC^{12}O_3^-$, ν_4 and ν_5 lie at 1211 and 960 cm^{-1}, respectively, and in $DC^{12}O_3^-$, ν_4 shifts to 975 cm^{-1}, but ν_5 is said to remain at 960 cm^{-1}. Naively, perhaps, a Fermi interaction is expected to shift ν_5 in $DC^{12}O_3^-$ to a lower frequency than in $HC^{12}O_3^-$. To test their assignments we have calculated Teller–Redlich product ratios for the six different combinations of the four sets of frequencies. The theoretical values of the ratios were obtained using the same structural parameters assumed by BHH, their set II. Excellent agreement, better than 1 part in 500, is obtained for the A″ modes for all cases, but the A′ assignments show several serious discrepancies summarized in Table IV.

TABLE IV

TELLER–REDLICH PRODUCT RATIOS FOR A′ FUNDAMENTALS OF HCO_3^- [a]

	Obsd	Theoret[c]
D12/H12[b]	0.594	0.517
D13/H13	0.594	0.516
H13/H12	0.945	0.939
D13/D12	0.945	0.938
D13/H12	0.561	0.485
D12/H13	0.629	0.551

[a] Data taken from Table II of ref 3. [b] Notation: H12, $HC^{12}O_3^-$; D13, $DC^{13}O_3^-$, etc. [c] Structural parameters are set II of ref 3.

The four cases in which the relative error in the product ratios is approximately 15% suggest that several of the assignments in the heavier species must be seriously in error. At least one of the two cases with moderately good agreement must be fortuitous, probably the one involving $DC^{13}O_3^-$ and $DC^{12}O_3^-$. We believe that the errors were caused by difficulty in selecting low wave number fundamentals in spectra of disks prepared by heating when excess potassium bicarbonate was present, and by lack of sufficiently good isotope purity. The enrichment of their carbon-13 source was only 57%, and they stated that their deuterated samples showed absorption due to hydrogen-containing species. Incorrect structural parameters are not the cause for disagreement because no reasonable change in the assumed parameters leads to agreement.

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[14] W. C. Price, W. F. Sherman, and G. R. Wilkinson, *Spectrochim. Acta*, **16**, 663 (1960).

[15] The symbol ν_3(KBr) means the third fundamental of the ion dispersed in KBr.