New Aromatic Anions. 11. Vibrational Spectra and Force Constants for Deltate Ion, $C_3O_3^{2-}$

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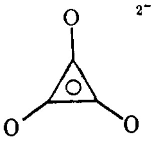
Abstract: The infrared and Raman spectra of the dilithium and dipotassium salt of the deltate ion, $C_3O_3^{2-}$ (**1**), are reported and analyzed. The results confirm D_{3h} symmetry for **1**. Normal coordinate analyses in both modified valence force field and Urey-Bradley models gave C-C and C-O stretching force constants which are consistent with increased C-C and decreased C-O bond orders in **1** compared to those in larger ring oxocarbon anions. The potential energy distribution among vibrational coordinates in **1** and the special features found in the solid-state spectra are discussed.

Recently we reported the synthesis of deltic acid and the deltate ion $C_3O_3^{2-}$ (**1**).[2a] The latter species is the three-membered ring anion in the oxocarbon series, which includes squarate (**2**), croconate (**3**), rhodizonate (**4**), and $C_6O_6^{4-}$ (**5**) ions.[2b]



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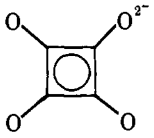

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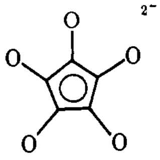

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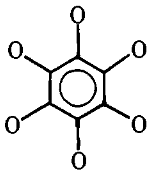

4, 2^-
5, 4^-

The predicted D_{4h} and D_{5h} symmetries of the squarate and croconate ions were initially confirmed by detailed analyses of their IR and Raman spectra.[3] Force constants obtained from the normal coordinate treatment of the vibrational spectra of squarate and croconate ions supported the view that compounds of the oxocarbon anions **2–4** should be considered an aromatic series.[2b,3] Subsequently, planar symmetrical structures were found for ions **2–4** by X-ray crystallography of dipotassium squarate monohydrate, diammonium croconate, and dirubidium rhodizonate.[2b] The bond lengths are consistent with cyclic π delocalization in these anions.

In this paper we report a vibrational study of deltate ion which confirms the D_{3h} symmetry proposed for this species. This is especially important because crystals suitable for X-ray study have not been obtained for deltate salts. In addition, a normal coordinate analysis of the vibrational spectra was carried out, permitting some conclusions to be drawn regarding bonding in **1** compared with other three-membered rings and with larger oxocarbon anions.

Experimental Section

Dilithium deltate (**1a**) was obtained by treating bis(trimethylsiloxy)cyclopropenone with lithium *tert*-butoxide at −78 °C, and conversion of **1a** to the dipotassium salt **1b** was effected by treatment with aqueous potassium fluoride. Both procedures were described in detail earlier.[2]

Infrared spectra in the normal region were determined on KBr and CsI pellets containing **1a** or **1b**, using a Perkin-Elmer 457 and a Beckman IR 4250 spectrometer. Far-infrared spectra were recorded on CsI pellets using a Digilab FTS-20 spectrometer (200-400 cm^{-1}) and on Nujol mulls using a Perkin-Elmer IR 180 instrument (100-600 cm^{-1}). Raman spectra were determined for aqueous lithium deltate solution, and for solid **1a** and **1b** in capillary tubes, using a Spex Ramalog-5 laser Raman spectrometer. The results are shown in Figures 1-3 and Tables I and II.

Vibrational Assignments. Assignments of fundamentals were made on the basis of D_{3h} symmetry (see Discussion section). In D_{3h} symmetry the 12 degrees of freedom ($3n - 6$, $n = 6$) are contained in eight normal modes, classified as $2a_1' + a_2' + a_2'' + 3e' + e''$ species (Table I). Atomic displacements corresponding to the normal modes are represented in Figure 4.[4] Assignment of frequencies to the different symmetry types is unambiguous because, as shown in Table I, each symmetry type gives rise to a different spectral activity.

a_1' Species. The totally symmetric vibrations are easily identified from the two polarized Raman lines of aqueous **1a** which lie at 1835 and 803 cm^{-1} (Tables I and II). The 1835-cm^{-1} absorption, ν_1, is rather weak for a totally symmetric Raman line. The corresponding Raman vibrations in **2** and **3** were also observed to be relatively weak.[3]

a_2'' Species. The a_2'' mode, ν_3, is an umbrella-like out of plane bending mode which is expected to be active only in the infrared. It is found in the IR spectrum of solid **1b** at 258 cm^{-1}.

e′ Species. Three additional in-plane modes (ν_5, ν_6, and ν_7) arise from combination of antisymmetric C-O stretching, C-C stretching, and in-plane C-O bending. These fundamentals, having e′ symmetry, are the only bands that should be found in both the Raman and IR spectra. In solid **1b**, three such bands are observed at 1432, 966, and 321 cm^{-1} in the Raman which correspond to absorptions at 1445, 965, and 325 cm^{-1} in the IR; these are assigned as the e′modes, ν_5, ν_6, and ν_7, respectively. The Raman lines are depolarized as predicted (Table II).

e″ Species. This final fundamental, a C-O out of plane bending mode, should be active in the Raman only and should be depolarized. Only one such Raman line is found in aqueous **1a**, at 696 cm^{-1}, and it therefore must be assigned to this species.

Other Observed Bands. In the infrared spectrum of solid **1b**, additional weak bands not listed in Table I were given the following assignments: 1105 cm^{-1}, $\nu_7 + \nu_2$; 1750, $\nu_6 + \nu_2$; 1942, $2 \times \nu_6$; and 2225, $\nu_5 + \nu_2$. In the infrared spectrum of solid **1a**, additional bands and their assignments follow: 272 (m), lattice mode (LM); 380 (s), LM; 425 (s), LM; 470 (s), LM; 3400, LM; 1381 (w), $2 \times \nu_8$; 1990 (w), $2 \times \nu_6$; 2300 (w), $\nu_5 + \nu_2$; 2834 (w), $\nu_1 + \nu_6$; 2960 (w), $2 \times \nu_5$. Additional bands observed in the Raman spectrum of **1b** are described in the Discussion section.

Correlation of Bending Modes of Oxocarbon Anions. The spectra of the squarate and croconate ions contain a number of bending modes. For each ion, two of these modes are in the 200-400-cm^{-1} range and are active only in the infrared. In their analysis of the spectra, Ito and West[3] tentatively assigned the higher frequencies (e_u and e_1') to in-plane C-O bendings and the lower frequencies (a_{2u} and a″) to out of plane C-O bendings. The deltate ion also has two C-O bending modes in this region, but is more definitely characterized since the in-plane

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Table I. Fundamental Vibrational Frequencies of the Deltate Ion

no.	symmetry type	activity	Raman, $Li_2C_3O_3$ (aq)	Raman, $K_2C_3O_3$ (s)	IR, $K_2C_3O_3$ (s)	IR, $Li_2C_3O_3$ (s)
ν_1	a_1'	R(P)	1835 m	1818 w		1830 w
ν_2	a_1'	R(P)	803 s	786 s		801 w
ν_3	a_2'	inactive				
ν_4	a_2''	IR			258 m	236 m
ν_5	e′	IR + R(dP)	1446 w	1432 w	1445 vs, br	1470 vs, br
ν_6	e′	IR + R(dP)	992 m	966 m	965 s	995, 972 s
ν_7	e′	IR + R(dP)	346 m	321 m	325 m	341 m
ν_8	e″	R(dP)	696 w	689 w		681 w

Table II. Raman Spectrum of Aqueous Dilithium Deltate

Raman shift, cm^{-1}	int	depol ratio	assign
346	59	0.714 (dP)	ν_7
696	6.0	0.75 (dP)	ν_8
803	100	0.078 (P)	ν_2
992	44	0.706 (dP)	ν_6
1446	4.5	0.66 (dP)	ν_5
1835	23	0.156 (P)	ν_1

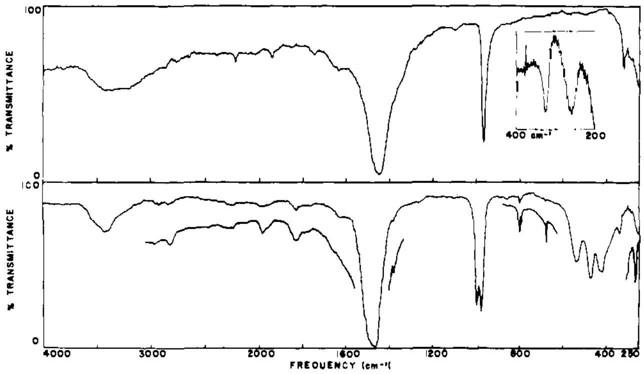

Figure 1. Above, infrared spectrum of solid dipotassium deltate in KBr pellet with the 200-400-cm^{-1} region (run in CsI) shown as an inset. Below, infrared spectrum of dilithium deltate, as KBr pellet with portions of the spectrum of a more concentrated CsI pellet.

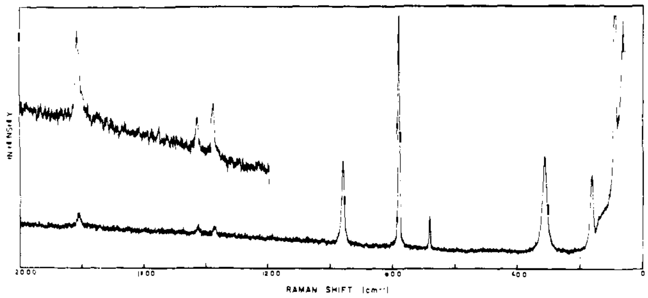

Figure 2. Raman spectrum of solid dipotassium deltate. The 1200-2000-cm^{-1} region is shown at higher detector sensitivity.

e′ mode is active in both IR *and* Raman spectra while the a_2'' mode appears only in the IR. The values of the deltate frequencies are compared to those assigned for squarate and croconate in Table III, clearly confirming the assignments previously made by Ito and West.[3]

Normal Coordinate Analysis. Based on the assignments discussed above and summarized in Table I, normal coordinate calculations were carried out both in modified valence force field and Urey-Bradley approximation. The bond lengths and angles assumed for the deltate anion were C-C = 1.40 Å, C-O = 1.212 Å, and CCO = 150°. Versions of the well-known normal coordinate programs of Schachtschneider[5] were used to solve the secular equation.

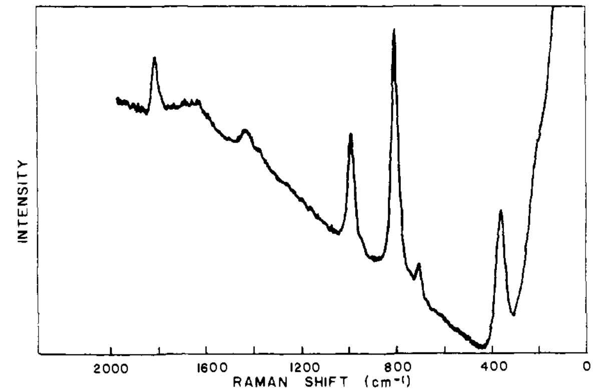

Figure 3. Raman spectrum of aqueous dilithium deltate solution.

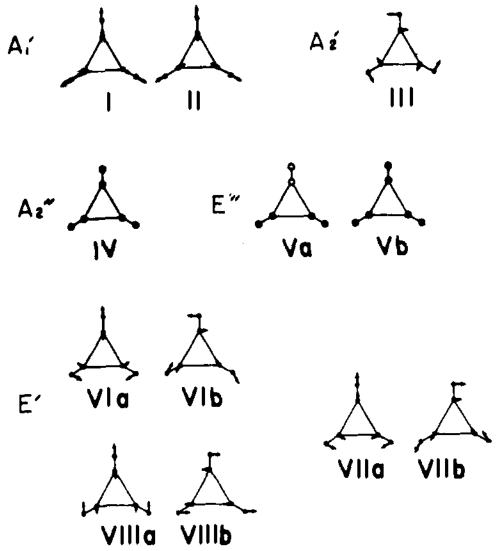

Figure 4. Normal modes of vibration for deltate ion.

Valence Force Field. Fifteen internal coordinates were chosen: the changes in the six bonds, the three out of plane angles, and the three in-plane angles depicted in Figure 5. Although the three CCC angles have been omitted, the sets chosen conform to the requirement that they be symmetrically complete. Cyvin and co-workers[6] have emphasized that the elimination of certain sets of symmetrically equivalent internal coordinates is a sound procedure and does not result in a loss of generality. The symmetry coordinates needed to describe the normal modes are listed in Table IV. Because there are more internal coordinates than symmetry coordinates, the transformation matrix is rectangular rather than square. However, this matrix still gives the correct factoring of the *G* and *F* matrices into symmetry blocks.[6,7]

Initial force constants in the valence force field were transferred from results of similar calculations on cyclopropenone[8] and subsequently refined in a least-squares fit to the observed frequencies. Seven

Table III. Bending Modes of Oxocarbon Anions

compd	sym	$\bar{\nu}$, cm^{-1}	assignment	sym	$\bar{\nu}$, cm^{-1}	assignment	sym	$\bar{\nu}$, cm^{-1}	assignment	ref
$C_5O_5^{2-}$	e_2'	555	ring bending	e_1'	374	in-plane C-O bend	a''	248	out of plane C-O bend	3
$C_4O_4^{2-}$	e_g	662	out of plane C-O bend	e_u	350	in-plane C-O bend	a_{2u}	259	out of plane C-O bend	3
	b_{2g}	647	ring bending							
$C_3O_3^{2-}$	e''	689	out of plane bend	e'	321	in-plane C-O bend	a_2''	258	out of plane C-O bend	this work

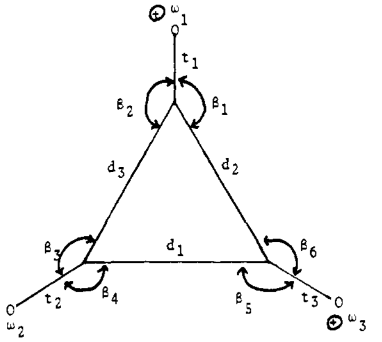

Figure 5. Internal coordinates for deltate ion.

Table IV. Symmetry Coordinates of Deltate Anion[a,b]

a'_1	$S_1 = (\Delta d_1 + \Delta d_2 + \Delta d_3)/\sqrt{3}$
	$S_2 = (\Delta t_1 + \Delta t_2 + \Delta t_3)/\sqrt{3}$
a'_2	$S_3 = (\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4 + \Delta\beta_5 - \Delta\beta_6)/\sqrt{6}$
a''_2	$S_4 = (\Delta\omega_1 + \Delta\omega_2 + \Delta\omega_3)/\sqrt{3}$
e'	$S_{5a} = (2\Delta d_1 - \Delta d_2 - \Delta d_3)/\sqrt{6}$
	$S_{6a} = (2\Delta t_1 - \Delta t_2 - \Delta t_3)/\sqrt{6}$
	$S_{7a} = (\Delta\beta_3 - \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6)/2$
	$S_{5b} = (\Delta d_2 - \Delta d_3)/\sqrt{2}$
	$S_{6b} = (\Delta t_2 - \Delta t_3)/\sqrt{2}$
	$S_{7b} = (2\Delta\beta_1 - 2\Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4 - \Delta\beta_5 + \Delta\beta_6)/\sqrt{12}$
e''	$S_{8a} = (2\Delta\omega_1 - \Delta\omega_2 - \Delta\omega_3)/\sqrt{6}$
	$S_{8b} = (\Delta\omega_2 - \Delta\omega_3)/\sqrt{2}$

[a] See Figure 5 for definition of internal coordinates. [b] S_3 corresponds to the inactive a'_2 mode.

Table V. Valence Force Constants[a]

$F_{11} = f_d + 2f_{dd} = 7.418$	$F_{55} = f_d - f_{dd} = 4.938$
$F_{22} = f_t = 7.990$	$F_{66} = f_t = 7.990$
$F_{12} = 2f_{dt} = 2.090$	$F_{77} = (f_\beta - f_{\beta\beta}) = 1.000^c$
$F_{33} = (f_\beta - f_{\beta\beta})^b$	$F_{56} = -f_{dt} = -1.045$
$F_{44} = f_\omega + 2f_{\omega\omega} = 0.415$	$F_{88} = f_\omega - f_{\omega\omega} = 0.728$

[a] See Table IV and Figure 5 for notations. Force constant units: stretch, mdyn/Å; bend, mdyn Å; stretch-stretch, mdyn/Å; bend-bend, mdyn Å. [b] Corresponding a'_2 mode is inactive. [c] Fixed during least-squares iteration.

independent force constants were found adequate to describe the system. During the least-squares fitting it was found that the diagonal (symmetry) force constant for the in-plane CCO bend must be constrained to obtain a convergent solution. This force constant was fixed at a value of 1.0 mdyn Å, a value close to the average of those found for the CCO in-plane bond in other cyclic ketones.[8,9]

Urey-Bradley Force Field. In the Urey-Bradley model, the G matrix was set up in the internal coordinate representation using the most complete set of 18 internal coordinates, namely, the 15 coordinates depicted in Figure 5 plus the displacements of the three apical CCC angles. The secular equation therefore yields six null roots corresponding to six redundancies.

To obtain a stable solution in the least-squares fit, the angle bending and repulsion force constants of the initial set had to be assumed markedly different from those found for **2** and **3**. Seven force constants were used excluding the repulsion constant F_{CC} which is necessarily zero in the Urey-Bradley model for a three-membered ring.

The set of converged values of the force constants for the valence force field is given in Table V; that for the Urey-Bradley is presented in Table VI along with comparison values for **2** and **3** and cyclopropenium ions. In both force fields the final set of force constants gave excellent agreement between calculated and observed frequencies (Table VII).

Discussion

The vibrational spectra confirm the D_{3h} structure proposed for deltate ion. The number and activities of the six strong Raman lines and four infrared bands assignable as fundamentals agree exactly with predictions based on D_{3h} symmetry.[4] Particularly significant is the fact that the Raman spectrum of aqueous **1a** showed only six lines (Figure 3) because possible lower symmetries (C_{2v}, C_2, or C_1) would give rise to at least 11 Raman-active fundamentals. These results establish that **1** has a symmetrical planar structure like the other oxocarbon anions.[2b]

The value for the C-C stretching force constant should provide useful information about bonding in the three-membered ring of **1**. In the valence force field, the value of this force constant as derived from the results in Table V is $f_d = 5.765$ mdyn/Å. Comparison values of f_d for related molecules using similar force fields follow: cyclopropane, 4.29[10] and 4.50;[11] cyclopropene, 4.48;[11] cyclopropenone, 5.6;[8] the aromatic triphenylcyclopropenium ion, 7.74.[12] Hence the valence force field results suggest that C-C π bonding in the deltate anion is more pronounced than in the other three-membered ring compounds, except for the highly aromatic triphenylcyclopropenium ion.

The extent of electron delocalization involving the carbonyl group and ring in **1** is also reflected in the lower value of the C-O stretching force constant (f_t = 7.99 mdyn/Å) compared to that of cyclopropenone (9.40 mdyn/Å) and the general range of 9-11 mdyn/Å for the C=O double bond in other cyclic ketones.[9]

Similarly, the Urey-Bradley force constants for the C-C stretch (K_{CC}) and C-O stretch (K_{CO}) summarized in Table VI are consistent with the pattern of increased C-O bond order and decreased C-C bond order with increasing ring size in the oxocarbon anion series. The angle bending and repulsion force constants also show the same trend found for **2** and **3**, although the differences between **1** and **2** are more pronounced than between **2** and **3**.

However, some difficulties arise in comparing the results of the UBFF calculation for **1** with those for **2** and **3**. Anion **2** has a relatively large value for F_{CC}, the nonbonded carbon-carbon repulsion constant. This constant in **2** and **3** expresses the interaction between adjacent C-C bond stretchings and between the C-C bond stretch and the CCC angle bending. Because this constant is necessarily zero in the Urey-Bradley treatment of **1**, interactions which would correspond to this

Table VI. Urey-Bradley Force Constants[a] (mdyn/Å)

	1	**2**	**3**	$C_3H_3^+$	$C_3Cl_3^+$	$C_3(CH_3)_3^+$
K_{CC}	5.565	3.95	3.50	6.590	6.221	6.315
K_{CO}	5.500	5.60	6.72			
H_{CCC}	−0.382	0.14	0.24	0.033	−0.484	−0.026
H_{CCO}	0.237	1.38	1.46			
F_{CO}	1.159	0.45	0.38			
F_{CC}	0[b]	3.91	1.52	0[b]	0[b]	0[b]
ref	this work	3	3	14	14	14

[a] Force constants relevant to the C-O out of plane bends (f_ω and $f_{\omega\omega}$) are the same as those found in the valence force field (see Table V). [b] F_{CC} is necessarily zero for a three-membered ring.

Table VII. Observed and Calculated Frequencies (cm^{-1})

	obsd	valence force field	Urey-Bradley
a′₁	1835	1831	1835
	803	810	802
a″₂	258	258	259
e′	1446	1446	1446
	992	992	992
	346	346	345
e′	696	696	696

Table VIII. Potential Energy Distribution among Symmetry Coordinates (Valence Force Field)

a′₁	ν_1 (1835)	ν_2 (803)	
C-C str (S_1)	68	21	
C-O str (S_2)	32	79	
e′	ν_5 (1446)	ν_6 (992)	ν_7 (346)
C-C str (S_5)	27	38	38
C-O str (S_6)	69	25	0
CCO bend (S_7)	4	37	62

force constant are absorbed in other Urey-Bradley force constants. In this connection, it is interesting to note that for **1**, as for other species with the same geometry,[13,14,15] the UBFF treatment gives an unexpected *negative* value for H_{CCC}. There are evidently ambiguities in the Urey-Bradley approximation for planar three-membered rings which are not fully understood.

However, even if a relatively large allowance is made for the effect of C-C stretch/C-C stretch interaction, it still appears that K_{CC} for **1** must be significantly higher than for **2** and **3**. This difference may reflect a shorter C-C distance, or greater π electron delocalization, or both, for **1** compared to the other oxocarbon anions.

The potential energy distribution among symmetry coordinates for the a₁′ and e′ modes as derived by the valence force field is given in Table VIII. Qualitatively similar potential energy distribution results from the Urey-Bradley calculations. The totally symmetric vibrations ν_1 = 1835 cm^{-1} and ν_2 = 803 cm^{-1} for the deltate anion can be respectively correlated with the frequency pairs 1794 and 723 cm^{-1} of **2** and 1718 and 637 cm^{-1} of **3**.[3] For the deltate anion, the higher frequency ν_1 is mainly C-C stretching with admixture of C-O stretching. Just the reverse is true for ν_2. Qualitative band assignments based solely on the range of characteristic frequencies normally associated with these functional groups will thus lead to an erroneous interpretation of the form of these vibrational modes. The Urey-Bradley calculations for **2** and **3**[3,17] indicate that ν_1 is also dominated by C-C terms and ν_2 by C-O in the case of $C_4O_4^{2-}$; both modes contain nearly equal admixture of C-C and C-O terms in $C_5O_5^{2-}$.

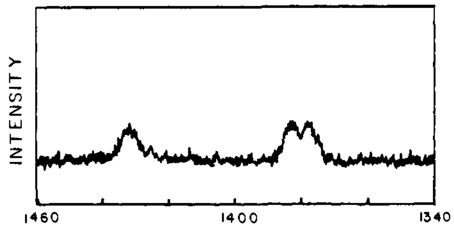

Figure 6. Part of the high-resolution Raman spectrum of solid dipotassium deltate (slits, 1.0 cm^{-1}).

Solid-State Spectra. The spectra of solid dipotassium and dilithium deltate contain extra bands which can be assigned as overtones, combination bands, lattice modes, and effects of reduced symmetry. The low-resolution (~5 cm^{-1}) Raman spectrum of solid dipotassium deltate has extra bands at 1381, 178, and 92 cm^{-1}. The two low-frequency bands disappeared when the sample was dissolved in water and can confidently be assigned as lattice modes. The overtone $2\nu_8$ is of symmetry species[18] A₁′ + E′, both components of which are Raman allowed. The surprising Raman intensity of this overtone is probably enhanced by Fermi resonance between its E′ component and the e′ fundamental, ν_5. This resonance may also be responsible for the doublet feature of the 1381-cm^{-1} band as seen in the high-resolution Raman spectrum (Figure 6), although a crystal field effect cannot be ruled out. If present, the same type of resonance should also be observed in the infrared as the E′ component is likewise infrared active. Although the low-frequency shoulder of the very strong ν_5 IR band at 1445 cm^{-1} indicates its possible presence, it could not be properly resolved to give a more definite proof.

The extra bands in the IR of dipotassium deltate enumerated earlier have all been assigned to overtones and combination bands. The suggested assignments can all be shown to have IR-active symmetries,[19] and the intensities are all much weaker than the four IR fundamentals (see Figure 1).

The IR spectrum of dilithium deltate (Figure 1) is much more complex, showing lattice modes and effects of reduced symmetry as well as overtones and combination bands. The e′ fundamentals are identified by comparison with solution Raman and dipotassium deltate IR and Raman data. The far-infrared spectrum contains two candidates at 236 and 272 cm^{-1} for ν_4, which is found in the IR spectrum of dipotassium deltate at 258 cm^{-1}. Because the Raman spectrum of solid dilithium deltate has a band at 272 cm^{-1}, the 236-cm^{-1} IR absorption is probably ν_4 (which is expected to be Raman inactive). The breakdown of D_{3h} symmetry, evidenced by the splitting of the e′ mode at ca. 1000 cm^{-1} into a double-peaked band, also allows ν_1, ν_2, and ν_8 to be weakly observed in the IR spectrum. The remaining weak bands have been given the overtone and combination band assignments listed in the Experimental Section.

Acknowledgment. The authors thank Professor Mitsuo Ito of Tohoku University for many helpful discussions. This work was supported in part by a grant from the National Science Foundation.

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A Theoretical Investigation of the Structure of $(Cl_2F)^+$ and Protonated ClF[1a]

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Received August 30, 1978

Abstract: In an attempt to resolve the controversy among experimentalists about the geometry of $(Cl_2F)^+$ cation, ab initio calculations have been carried out on the ground states of $(ClFCl)^+$ and $(ClClF)^+$ within the framework of the restricted Hartree-Fock theory. For comparison purposes, similar calculations have been performed on $(HFCl)^+$ and $(HClF)^+$. We find that, using 44-31G type basis sets, $(ClFCl)^+$ is more stable than $(ClClF)^+$, and $(HFCl)^+$ is more stable than $(HClF)^+$. The results of theoretical calculations are interpreted using Mulliken's population analysis, Morokuma's energy decomposition analysis, and the configuration analysis of Baba et al. Optimized geometries are presented for all of these molecular ions.

I. Introduction

Christe and Sawodny (CS) have shown that a new oxidizing species, $(Cl_2F)^+$, is formed in the form of a salt when ClF reacts with AsF_5 or BF_3:[2a]

$$AsF_5 + 2ClF \rightarrow (Cl_2F)^+(AsF_6)^-$$

$$BF_3 + 2ClF \rightarrow (Cl_2F)^+(BF_4)^-$$

The existence of such salts containing the novel cation, $(Cl_2F)^+$, has been confirmed by the work of Gillespie and Morton (GM).[2b] In their original paper reporting the discovery of $(Cl_2F)^+$ CS suggested that the ion was most likely to be a bent C_{2v}-symmetry molecule, $(ClFCl)^+$, with a bond angle of about 100–120°. This conclusion was challenged by GM, who suggested that $(Cl_2F)^+$ has the asymmetric, $(ClClF)^+$, structure. There has been an attempt to rationalize this suggested asymmetric structure of $(Cl_2F)^+$ using arguments based upon the frontier orbital concept.[3]

In this paper we present the results of our theoretical investigation of the structure of $(Cl_2F)^+$ using ab initio molecular orbital theory. We have also investigated the structure of protonated ClF for comparison purposes. Both of these cations can be thought of as products of interaction between ClF and the ion Cl^+ or H^+.

II. Ab Initio Geometry and Stabilization Energies

Using the standard split-valence basis set, 44-31G,[4a] with the recommended exponents and scale factors,[5] we have carried out ab initio calculations on Cl^+, ClF, $(ClFCl)^+$, $(ClClF)^+$, $(HClF)^+$, and $(ClFH)^+$ within the framework of closed-shell single-determinant Hartree-Fock theory. All geometrical parameters were optimized. The total energies, optimum geometrical parameters, and the binding energies of $(ClFCl)^+$, $(ClClF)^+$, $(ClFH)^+$, and $(HClF)^+$ are given in Table I. These results show that both $(ClFCl)^+$ and $(ClClF)^+$ are stable species with respect to isolated Cl^+ and ClF. The stability of $(ClFCl)^+$ is about 10 kcal/mol higher than that of $(ClClF)^+$. The $(ClFCl)^+$ ion has C_{2v} symmetry with a large bond angle of 140°. Our calculations show that all non-C_{2v}-symmetry structures for $(ClFCl)^+$ have higher energies. The $(ClClF)^+$ ion has a rather small bond angle of 99°.

It is interesting to note that a limited basis set, STO-3G, with recommended exponents and scale factors[4b] shows that $(ClClF)^+$ is more stable than $(ClFCl)^+$ by about 8 kcal/mol. The limited basis set also gives a rather different bond angle for $(ClFCl)^+$, although other geometrical parameters for these two cations are similar to those obtained by using the more flexible 44-31G basis. This suggests that the relative stabilities

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