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A High-Resolution Fourier Transform Infrared Study of the ν_3, ν_4, and ν_5 Bands of Deuterated Formyl Chloride (DCOCl)

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High-resolution infrared spectra of the low-lying ν_3, ν_4, and ν_5 fundamentals of the transient molecule DCOCl are reported. These type-A/B hybrid bands have been analyzed in detail, providing extensive rotational assignments for the $DCO^{35}Cl$ and $DCO^{37}Cl$ isotopomers. The ground state constants have been refined by a simultaneous fit of the available microwave data and FTIR combination differences from the three bands. The excited state constants have been determined by fitting assignments over a wide range of J and K_a values. A small perturbation was found at high K_a values in the ν_4 band and determined to be due to a $\Delta K_a = -2$ interaction with the rotational levels of the 6^1 vibrational state.

INTRODUCTION

Formyl chloride is a transient molecule which readily decomposes into HCl and CO. It is of importance in two types of upper atmospheric reactions involving chlorinated alkenes. Chloroethenes such as vinyl chloride and trichloroethene are released into the atmosphere in large quantities and they are degraded primarily by reactions with OH radicals (*1, 2*). Formyl chloride has been shown by long pathlength FTIR absorption spectroscopy to be a major product of such reactions (*3*). It has also been shown that formyl chloride is a product of the gas-phase reaction of ozone with a variety of chloroethenes (*4, 5*). In other contexts, formyl chloride is thought to be involved in the Gattermann–Koch reaction for the formylation of aromatic hydrocarbons (*6*). It is also produced in the photochlorination of formaldehyde (*7*) and the chlorine atom sensitized oxidation of methylene chloride and chloroform (*8, 9*).

Formyl chloride was first reported by Krauskopf and Rollefson (*10*) and subsequently characterized by low-resolution infrared spectroscopy (*11*). Microwave work by a variety of groups (*12–16*) resulted in a thorough description of the ground state, including the accurate determination of rotational and centrifugal distortion constants from data over a wide range of J and K_a. Recently, we embarked on a program to study the high-resolution infrared spectra of formyl chloride. The ν_3 (in-plane bending fundamental) bands of $HCO^{35}Cl$ and $HCO^{37}Cl$ at 1307 cm^{-1} were recorded at natural abundance and analyzed in detail (*17*). The bands are type-A/B hybrids, with the A-type component about four times stronger than the B-type. The ground state constants of both isotopomers were refined using infrared combination differences and the available microwave data. The excited state constants were determined and a few minor perturbations were observed at high values of J' and K'_a. The ν_2 band at 1784 cm^{-1}

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was found to be predominantly *A*-type, with extensive Fermi and Coriolis perturbations by interactions with the nearby $3^1 5^1$ vibrational state (*18*). A complete analysis of the band was possible using a Hamiltonian which accounts for both interactions, yielding molecular constants for the bright 2^1 and the dark $3^1 5^1$ vibrational states. Most recently, we reported the analysis of the low-lying ν_4 and ν_5 fundamentals of HCOCl at 738.8 and 457.0 cm^{-1} (*19*). The excited state rotational and centrifugal distortion constants were determined by fitting assignments over a wide range of J and K_a values. As expected, both bands were free of detectable perturbations.

In the present work, we report the analysis of the ν_3, ν_4, and ν_5 bands of deuteroformyl chloride (DCOCl). Extensive infrared combination differences from all three bands have been combined with the available microwave data to refine the ground state constants. The bands are almost completely free of excited state perturbations and were fitted to give accurate upper state molecular constants.

EXPERIMENTAL DETAILS

The FTIR spectrometer was a Bomem DA3.002 interferometric spectrophotometer equipped with a globar light source. DCOCl was slowly pumped through a Wilks-type variable pathlength multiple reflection cell. The spectra were recorded at full resolution and then transformed with a Hamming apodization function to give an effective resolution of ≈ 0.004 cm^{-1}. In order to simplify the spectra, we have deconvoluted them to an effective resolution of ca. 0.002 cm^{-1}, as described in earlier work (*17*). The spectra were calibrated using known lines of reference gases (*20*) recorded under the same instrumental conditions during or immediately after recording the DCOCl spectra. The experimental parameters used for each band are summarized in Table I.

Deuteroformyl chloride was produced by the reaction of DCOOD (Merck, Sharpe and Dohme 98% isotopic purity) vapor with granular phosphorus pentachloride, as previously described (*17*).

RESULTS AND DISCUSSION

Formyl chloride is a planar molecule of C_s symmetry with five a' and one a'' fundamentals. The low resolution mid-infrared spectrum of essentially pure DCOCl is

TABLE I

Experimental Parameters for the FTIR Spectra of DCOCl

	Band		
Parameter	ν_3	ν_4	ν_5
Pressure (Torr)	1.5	0.4	1.2
Pathlength (m)	8.25	5.25	8.25
# of scans	128	80	108
Detector	MCT[a]	Cu:Ge[b]	Cu:Ge[b]
Beamsplitter	KCl	Mylar	Mylar
Calibration gas (Torr)	OCS (0.3)	CO_2 (0.2)	H_2O in spectrometer

[a]Mercury-cadmium-telluride detector.

[b]Copper-doped germanium detector.

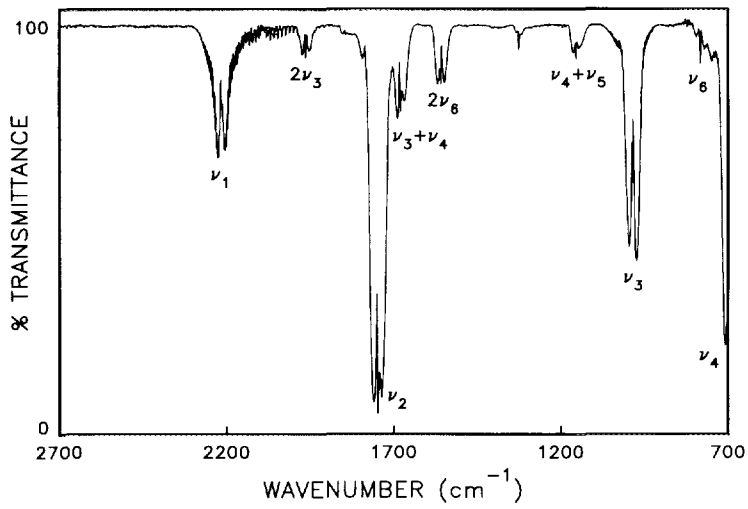

FIG. 1. Low-resolution transmittance spectrum of DCOCl in the 700–2700 cm^{-1} region.

given in Fig. 1. The ν_1–ν_4 fundamentals consist of a strong central type-*A* component and weaker type-*B* structure in the wings; their assignments follow readily from the force field calculations of Ref. (*16*). The other *a'* fundamental, ν_5, with a similar band contour, was observed at 456 cm^{-1}. A weak band at 782 cm^{-1} with a *C*-type band contour was assigned as ν_6. A variety of overtone and combination bands were also identified, as summarized in Table II.

The moderately strong CD bending fundamental, ν_3, lies in the 920–1050 cm^{-1} region, as shown in Fig. 2. At high resolution, the very intense central *Q* branch does

TABLE II

Vibrational Frequencies of DCOCl (in cm^{-1})

Vibration	$DCO^{35}Cl$	$DCO^{37}Cl$
ν_1(a') (CD stretch)	2204.3[a]	~2204[a]
ν_2(a') (CO stretch)	1749.1[a]	~1749[a]
ν_3(a') (CD bend)	986.1122[b]	986.0701[b]
ν_4(a') (CCl stretch)	700.7738[b]	697.4841[b]
ν_5(a') (CCl bend)	455.7784[b]	451.3893[b]
ν_6(a'') (out-of-plane bend)	782.0[a]	~782[a]
$2\nu_3$	1962.7[a] (2 × 986.1 = 1972.2)	
$2\nu_6$	1557.0[a] (2 × 782.0 = 1564)	
$\nu_4 + \nu_5$	1153.9[a] (700.8 + 455.8 = 1156.6)	
$\nu_3 + \nu_4$	1679.2[a] (986.1 + 700.8 = 1686.9)	

[a]Estimated from our low-resolution spectrum, Fig. 1.

[b]This work.

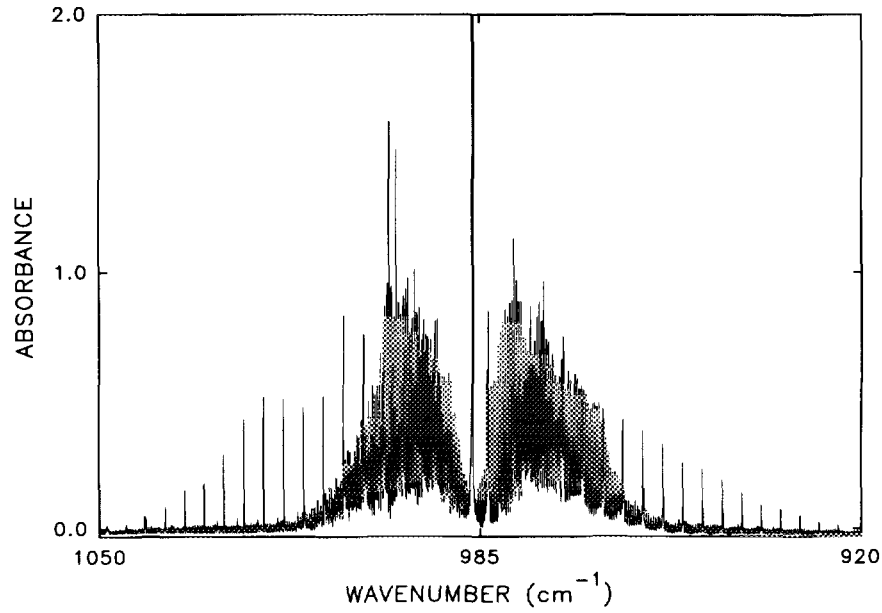

FIG. 2. The type-A/B hybrid fundamental band ν_3 of DCOCl.

not show resolved rotational structure or isotope splittings, which indicates quite small changes in the rotational constants on excitation. The type-A P- and R-branch lines form easily identifiable clusters of lines of the same J and different K_a, as shown in

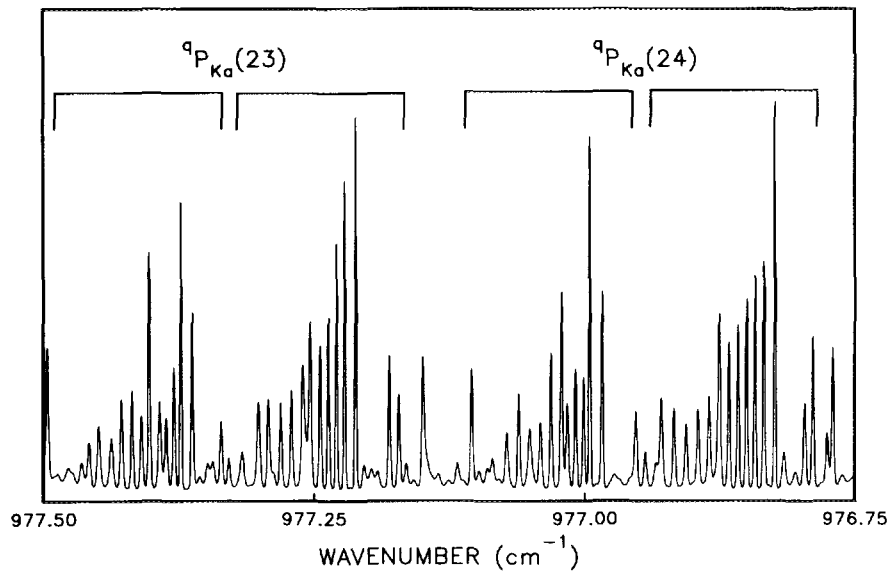

FIG. 3. A portion of the A-type rotational structure of the ν_3 band of DCOCl at high resolution, showing the chlorine isotope structure. In each case, the group of lines at higher wavenumbers belongs to the DCO^{37}Cl isotopomer.

Fig. 3. This made assignments relatively straightforward in the regions where the blending of lines was minimal. The assignment process was begun with the weak ^qR lines of DCO^{35}Cl just beyond the central Q branch; these were confirmed by forming combination differences with the corresponding ^qP lines. In this fashion, assignments were made up to $K_a = 16$ with a maximum $J = 65$ for the strongest branches.

Once the DCO^{35}Cl A-type structure had been assigned and a reliable set of upper state rotational constants obtained, the type-B lines in the wings of the band could be assigned. The type-B component, which appears at the sides of Fig. 2, displays a series of prominent, though mostly unresolved, Q branches along with weaker P and R branches in the wings of the band. For $K'_a = 5$–16 it was possible to assign the stronger ^rR and ^pP branches, as well as some of the ^rQ- and ^pQ-branch lines. The B-type lines were very useful in obtaining precise values of the A, Δ_k, and H_K state constants in both the upper and lower states.

Once all of the DCO^{35}Cl lines had been identified, the assignment of the DCO^{37}Cl spectrum was attempted. In the ν_3 band, the isotope shift is small (0.04 cm^{-1}) and the A-type lines fall between the corresponding clusters of lines in the DCO^{35}Cl spectrum, as illustrated in Fig. 3, so that the assignments were less difficult to make than in the other bands. The weaker B-type lines were also assignable for intermediate values of K_a.

The ν_4 and ν_5 bands were more difficult to assign, because of extensive line overlap and congestion. The ν_4 band, shown in Fig. 4, does not exhibit prominent B-type structure at low resolution, although the lines are readily identified in the high-resolution spectra. The large isotope effect (3.3 cm^{-1}) for this CCl stretching vibration complicates matters since the weaker low-J ^qR lines of the DCO^{35}Cl isotopomer are overlapped by stronger lines of the DCO^{37}Cl species, so that the two are hard to distinguish. The starting point for the analysis was the weak ^qP lines of DCO^{35}Cl near the central Q

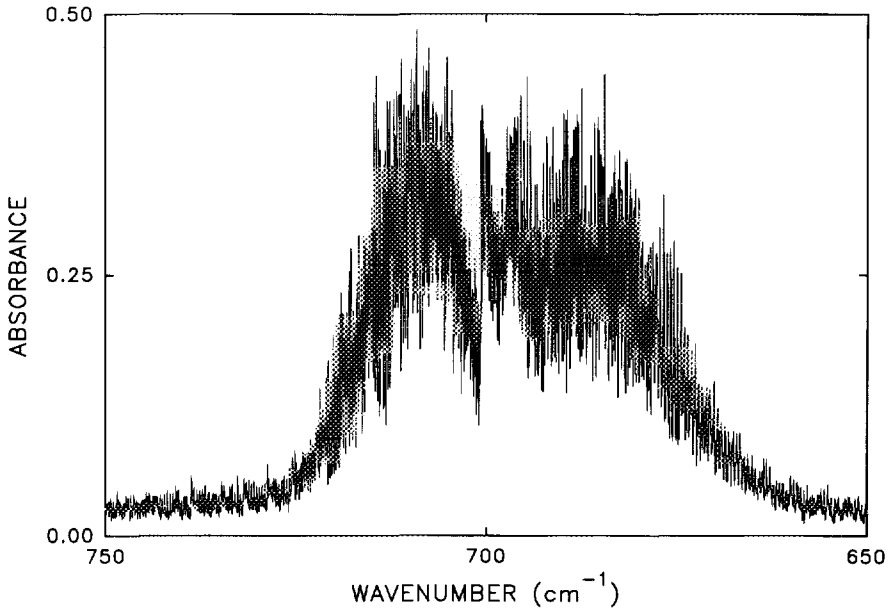

FIG. 4. Type-A rotational structure in the ν_4 band of DCOCl. The type-B component is very weak.

branch where the interference from the other isotope is slight. The A-type Q-branch lines were well-resolved above $K_a = 3$, so that the initial assignments were readily confirmed by ground state combination differences. Subsequently, the B-type lines were identified, providing assignments up to $K'_a = 18$. The spectrum of the $DCO^{37}Cl$ isotopomer was also assigned over a smaller range of K'_a values.

The ν_5 band, shown in Fig. 5, was the most difficult to analyze because of its weakness and the substantial line overlapping that results from the large chlorine isotope shift (4.39 cm^{-1}). As in the ν_5 band of HCOCl (*19*), the Q branches are blue-degraded, reflecting an increase in the quantity $(A - \bar{B})$ on excitation. The spectrum was analyzed in a manner very similar to that of the ν_4 band, although fewer lines could be assigned. The type-B component of the ν_5 fundamental is very weak and could not be found for the $DCO^{37}Cl$.

In the course of the analysis, it was found that the available ground state constants (*16*) were not sufficiently precise to reproduce the observed ground state combination differences at high K_a values. Once all the assignments were complete, the ground state constants were refined by a simultaneous, weighted least-squares fitting of the available microwave data (*16*) and combination differences obtained from the A- and B-type transitions of all three bands for each isotopomer. The transitions were weighted as the square of the inverse of the precision of the measurements, with the microwave lines given a precision of 0.05 MHz and the FTIR measurements 0.0004 cm^{-1}. A total of 73 microwave lines and 11 652 infrared combination differences were used for $DCO^{35}Cl$; 29 microwave lines and 2664 infrared combination differences were used for $DCO^{37}Cl$. Watson's A-reduction (*21*) of the asymmetric-top Hamiltonian in the I^r representation was used in fitting the data and the resulting ground state molecular constants are given in Tables III and IV. The constants are very similar to those reported in Ref. (*16*) from microwave data, but the standard deviations have been significantly improved.

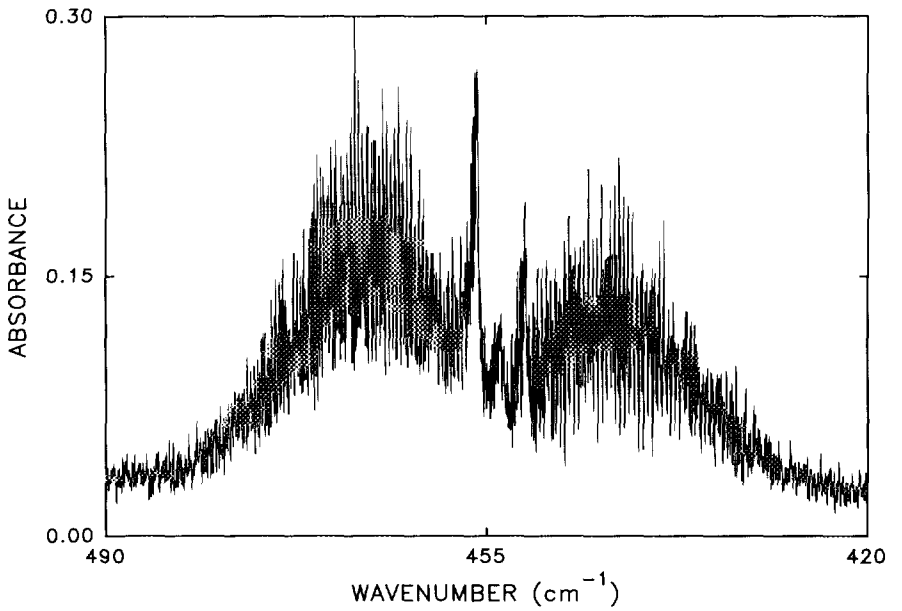

FIG. 5. The ν_5 band of DCOCl.

TABLE III

Rotational and Centrifugal Distortion Constants of $DCO^{35}Cl$ (in cm^{-1})

	Ground State		3^1 State	4^1 State	5^1 State
	Microwave Data[a]	Combined Data[b]			
Rotational constants					
A	1.90398892(27)	1.90398897(25)	1.90443891(39)	1.89205001(53)	1.91260913(81)
B	0.20347968(3)	0.203479695(27)	0.203835275(45)	0.202557648(54)	0.202972228(55)
C	0.18358354(3)	0.183583542(26)	0.183245714(46)	0.182679538(56)	0.182961077(58)
Centrifugal distortion constants					
$10^5\ \Delta_K$	3.6572(23)	$3.65139_5(19)$	3.66219(29)	3.46398(42)	3.7779(10)
$10^7\ \Delta_{JK}$	-8.605(21)	$-8.5391_8(18)$	-9.5124(17)	-9.5252(37)	-8.4075(34)
$10^7\ \Delta_J$	1.139(1)	$1.14144_6(12)$	1.15990(20)	1.14687(22)	1.16178(24)
$10^7\ \delta_K$	6.6409(47)	$6.6447_4(49)$	8.320(13)	5.173(16)	7.306(17)
$10^8\ \delta_J$	1.506(1)	$1.50817_2(16)$	1.58621(50)	1.51337(65)	1.54745(65)
$10^9\ H_K$	3.2(5)	$2.3581_5(41)$	2.3925(64)	2.0169(83)	2.6097(35)
$10^{10}\ H_{KJ}$	-1.61(18)	$-1.3040_2(86)$	-0.8012(65)	-2.400(27)	-1.341(21)
H_{JK}	0.0[c]	0.0[c]	0.0[c]	0.0[c]	0.0[c]
$10^{14}\ H_J$	2.6(6)	$3.50_5(19)$	5.85(34)	9.40(37)	1.79(40)
h_K	0.0[c]	0.0[c]	0.0[c]	0.0[c]	0.0[c]
$10^{12}\ h_{JK}$	3.3(3)	$3.01_3(26)$	3.013[d]	3.013[d]	3.013[d]
$10^{14}\ h_J$	1.7(1)	$1.933_4(81)$	1.9334[d]	1.9334[d]	1.9334[d]
T_0			986.11220(2)	700.77379(2)	455.77838(2)
Std. Dev.[e]			0.00024	0.00028	0.00028

[a]Values converted from Ref. 16, using $c = 2.99792458 \times 10^{10}$ cms^{-1}. The error limits are 1σ and are right justified to the last digit quoted.

[b]A weighted least squares fit of microwave transitions (Ref. 16) and combination differences from the ν_3, ν_4, and ν_5 infrared bands was used to determine the constants; sufficient additional digits are quoted below the line to reproduce the original data with full accuracy.

[c]Constrained.

[d]Constrained to the ground state value of $DCO^{35}Cl$.

[e]Overall standard deviation of fit in cm^{-1}.

Once the ground state constants were determined from the pooled data, the excited state constants were obtained for each individual band. The ground state constants were fixed at the values given in Tables III and IV and the upper state constants were varied in a simultaneous fit of the *A*- and *B*-type transitions for each isotopomer. In order to ensure that badly overlapped or perturbed lines were not included in the least-squares fitting, only lines with residuals (obs − calc) less than 0.0005 cm^{-1} were retained in the final analysis. The resulting molecular constants are given in Tables III and IV. In all cases, the excited state constants are of the same sign and order of magnitude as the ground state constants and are otherwise unremarkable. The observed

TABLE IV

Rotational and Centrifugal Distortion Constants of $DCO^{37}Cl$ (in cm^{-1})

	Ground State		3^1 State	4^1 State	5^1 State
	Microwave Data[a]	Combined Data[b]			
Rotational constants					
A	1.9014578(4)	1.90145886(43)	1.90187165(65)	1.8902375(11)	1.9098813(15)
B	0.19876576(5)	0.198765837(42)	0.199097849(87)	0.197879729(76)	0.19826451(10)
C	0.17971478(5)	0.179714845(39)	0.179384121(84)	0.178837023(73)	0.17910734(10)
Centrifugal distortion constants					
$10^5\ \Delta_K$	3.6345(60)	3.63634_3(48)	3.64093(54)	3.4613(13)	3.7732(18)
$10^7\ \Delta_{JK}$	-8.412(53)	-8.4149_7(52)	-9.3601(41)	-9.3378(69)	-8.231(10)
$10^7\ \Delta_J$	1.093(2)	1.09363_2(19)	1.11003(18)	1.09544(12)	1.11134(24)
$10^7\ \delta_K$	6.4001(70)	6.4076_8(56)	8.118(44)	5.175(32)	6.703(71)
$10^8\ \delta_J$	1.416(1)	1.41565_7(21)	1.4960(16)	1.4189(12)	1.4845(22)
$10^9\ H_K$	3.2(5)	2.412_3(14)	2.293(13)	1.647(40)	3.086(55)
$10^{10}\ H_{KJ}$	-1.61(18)	-1.427_9(34)	-1.067(18)	-2.137(50)	-1.311(82)
H_{JK}	0.0[c]	0.0[c]	0.0[c]	0.0[c]	0.0[c]
$10^{14}\ H_J$	2.6(6)	3.505[d]	3.505[d]	3.505[d]	3.505[d]
h_K	0.0[c]	0.0[c]	0.0[c]	0.0[c]	0.0[c]
$10^{12}\ h_{JK}$	3.3(3)	3.013[d]	3.013[d]	3.013[d]	3.013[d]
$10^{14}\ h_J$	1.7(1)	1.9334[d]	1.9334[d]	1.9334[d]	1.9334[d]
T_0			986.07007(2)	697.48408(3)	451.38925(3)
Std. Dev.[e]			0.00026	0.00030	0.00029

[a]Values converted from Ref. 16, using $c = 2.99792458 \times 10^{10}\ cms^{-1}$. The error limits are 1σ and are right justified to the last digit quoted.

[b]A weighted least squares fit of microwave transitions (Ref. 16) and combination differences from the ν_3, ν_4, and ν_5 infrared bands was used to determine the constants; sufficient additional digits are quoted below the line to reproduce the original data with full accuracy.

[c]Constrained.

[d]Constrained to the ground state value of $DCO^{35}Cl$.

[e]Overall standard deviation of fit in cm^{-1}.

band origins and isotope shifts are in reasonable accord with the predictions of the harmonic force field obtained by Davis and Gerry (*16*).

The only perturbations observed in the three bands occur at high K'_a values in the ν_4 fundamentals of the two chlorine isotopomers; the residuals from the least-squares fits for $DCO^{35}Cl$ are shown in Fig. 6. The way the shifts rise to a maximum at $K_a = 13$, change sign at $K_a = 14$, and then diminish suggests an interaction with a single vibrational level by a mechanism with $\Delta K_a \neq 0$. From Table II, the only possibility for the perturbing level is ν_6, which was identified by its weak Q branch at 782 cm^{-1} in the low-resolution spectrum; from the rotational constants, the selection rule must be $\Delta K_a = \pm 2$. In a molecule of C_s symmetry, levels of a'' symmetry, such as ν_6, can interact with levels of a' symmetry, such as ν_4, through a- or b-axis Coriolis coupling

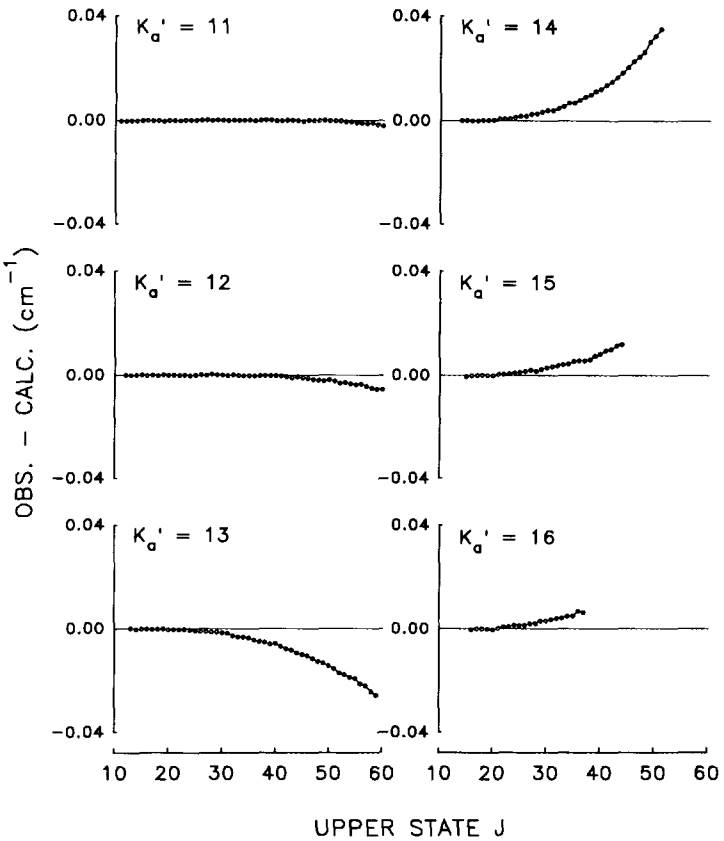

FIG. 6. Systematic shifts in the higher K_a rotational levels of the 4^1 state of $DCO^{35}Cl$ caused by a $\Delta K_a = \pm 2$ interaction with the ν_6 fundamental.

with the selection rules $\Delta K_a = 0, \pm 2, \cdots$ or $\Delta K_a = \pm 1, \pm 3, \ldots$, respectively. In this case, the $K_a = 11$ levels of 6^1 lie slightly above $K_a = 13$ of ν_4, causing the negative residuals. At higher energy the situation is reversed with $K_a = 12$ of 6^1 lying below $K_a = 14$, causing the positive residuals. The small level shifts observed are consistent with the size of the matrix elements expected for $\Delta K_a = \pm 2$ perturbations (*18*) in formyl chloride. It is gratifying that such small perturbations can be detected in such a complex spectrum.

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