A High-Resolution Fourier Transform Infrared Study of the $\nu_3$, $\nu_4$, and $\nu_5$ Bands of Deuterated Formyl Chloride (DCOCI)

DENNIS J. CLOUTHIER,* † C. P. CHAN, † A. J. MERER, † AND R. H. JUDGE‡

*Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055; † Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Y6, Canada; and ‡Department of Chemistry, University of Wisconsin–Parkside, Kenosha, Wisconsin 53141-2000

High-resolution infrared spectra of the low-lying $\nu_3$, $\nu_4$, and $\nu_5$ 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 $\nu_4$ band and determined to be due to a $\Delta K_a = -2$ interaction with the rotational levels of the $6^1$ vibrational state. © 1995 Academic Press, Inc.

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 Rolleson (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 $\nu_3$ (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 $\nu_2$ band at 1784 cm$^{-1}$

$^1$ To whom correspondence should be addressed.
was found to be predominantly $A$-type, with extensive Fermi and Coriolis perturbations by interactions with the nearby $3^1S^1$ 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 $3^1S^1$ vibrational states. Most recently, we reported the analysis of the low-lying $v_4$ and $v_5$ 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 $v_3$, $v_4$, and $v_5$ 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 $\approx 0.004$ 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 $C_2$ symmetry with five $a'$ and one $a''$ fundamentals. The low resolution mid-infrared spectrum of essentially pure DCOCl is

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$v_3$</th>
<th>$v_4$</th>
<th>$v_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (Torr)</td>
<td>1.5</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Pathlength (m)</td>
<td>8.25</td>
<td>5.25</td>
<td>8.25</td>
</tr>
<tr>
<td># of scans</td>
<td>128</td>
<td>80</td>
<td>108</td>
</tr>
<tr>
<td>Detector</td>
<td>MCT*</td>
<td>Cu:Ge*</td>
<td>Cu:Ge*</td>
</tr>
<tr>
<td>Beamsplitter</td>
<td>KCl</td>
<td>Mylar</td>
<td>Mylar</td>
</tr>
<tr>
<td>Calibration gas (Torr)</td>
<td>OCS (0.3)</td>
<td>CO$_2$ (0.2)</td>
<td>H$_2$O in spectrometer</td>
</tr>
</tbody>
</table>

*Mercury-cadmium-telluride detector.

*Copper-doped germanium detector.
given in Fig. 1. The $\nu_1 - \nu_6$ 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 $a^\prime$ fundamental, $\nu_5$, 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 $\nu_6$. A variety of overtone and combination bands were also identified, as summarized in Table II.

The moderately strong CD bending fundamental, $\nu_3$, lies in the 920–1050 cm$^{-1}$ region, as shown in Fig. 2. At high resolution, the very intense central $Q$ branch does

<table>
<thead>
<tr>
<th>Vibration</th>
<th>DCO$^6$Cl</th>
<th>DCO$^7$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1(a')$ (CD stretch)</td>
<td>2204.3$^a$</td>
<td>~2204$^a$</td>
</tr>
<tr>
<td>$\nu_2(a')$ (CO stretch)</td>
<td>1749.1$^a$</td>
<td>~1749$^a$</td>
</tr>
<tr>
<td>$\nu_3(a')$ (CD bend)</td>
<td>986.1122$^b$</td>
<td>986.0701$^a$</td>
</tr>
<tr>
<td>$\nu_4(a')$ (CCl stretch)</td>
<td>700.7738$^b$</td>
<td>697.4841$^b$</td>
</tr>
<tr>
<td>$\nu_5(a')$ (CCl bend)</td>
<td>455.7784$^a$</td>
<td>451.3893$^a$</td>
</tr>
<tr>
<td>$\nu_6(a')$ (out-of-plane bend)</td>
<td>782.0$^a$</td>
<td>~782$^a$</td>
</tr>
</tbody>
</table>

$2\nu_3$ | 1962.7$^a$ (2 x 986.1 = 1972.2) |

$2\nu_4$ | 1557.0$^a$ (2 x 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.
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

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**Fig. 3.** A portion of the $A$-type rotational structure of the $v_2$ band of DCOCI at high resolution, showing the chlorine isotope structure. In each case, the group of lines at higher wavenumbers belongs to the DCO$^{35}$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 $^pP$ 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 $^qR$ and $^pP$ branches, as well as some of the $Q$- and $P$-branch lines. The $B$-type lines were very useful in obtaining precise values of the $A$, $\Delta_k$, 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 $\nu_3$ 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 $\nu_4$ and $\nu_5$ bands were more difficult to assign, because of extensive line overlap and congestion. The $\nu_4$ 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$^{33}$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 $\nu_4$ 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$^{35}$Cl isotopomer was also assigned over a smaller range of $K_a'$ values.

The $v_5$ 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 $v_5$ band of HCOCI (19), the $Q$ branches are blue-degraded, reflecting an increase in the quantity $(A - B)$ on excitation. The spectrum was analyzed in a manner very similar to that of the $v_4$ band, although fewer lines could be assigned. The type-$B$ component of the $v_5$ fundamental is very weak and could not be found for the DCO$^{35}$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 $j'$ 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.
## TABLE III
Rotational and Centrifugal Distortion Constants of DCO\(^{13}\)Cl (in \(\text{cm}^{-1}\))

<table>
<thead>
<tr>
<th>Ground State</th>
<th>Microwave Data(^a)</th>
<th>Combined Data(^b)</th>
<th>3(^1) State</th>
<th>4(^1) State</th>
<th>5(^1) State</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.90398892(27)</td>
<td>1.90398897(25)</td>
<td>1.90443891(39)</td>
<td>1.89205001(53)</td>
<td>1.91260913(81)</td>
</tr>
<tr>
<td>B</td>
<td>0.20347968(3)</td>
<td>0.203479695(27)</td>
<td>0.203835275(45)</td>
<td>0.202557648(54)</td>
<td>0.202972228(55)</td>
</tr>
<tr>
<td>C</td>
<td>0.18358354(3)</td>
<td>0.183583542(26)</td>
<td>0.183245714(46)</td>
<td>0.182679538(56)</td>
<td>0.18264077(58)</td>
</tr>
</tbody>
</table>

### Centrifugal distortion constants

\[
\begin{array}{cccc}
10^4 \Delta \kappa & 3.6572(23) & 3.65139_{(19)} & 3.66219(29) & 3.46398(42) & 3.7779(10) \\
10^6 \Delta \kappa & -8.605(21) & -8.539_{(18)} & -9.5124(17) & -9.5252(37) & -8.4075(34) \\
10^4 \Delta \lambda & 1.139(1) & 1.14144_{(12)} & 1.15990(20) & 1.14687(22) & 1.16178(24) \\
10^6 \Delta \lambda & 6.640_{(47)} & 6.6447_{(49)} & 6.820(13) & -5.173(16) & 7.306(17) \\
10^4 \Delta \delta & 1.506(1) & 1.50817_{(16)} & 1.58621(50) & 1.51337(65) & 1.54745(65) \\
10^6 \Delta \delta & 3.2(5) & 2.3581_{(41)} & 2.3925(64) & 2.0169(83) & 2.6097(35) \\
10^4 \Delta \zeta & -1.61(18) & -1.3040_{(86)} & 0.0812(65) & 0.2400(27) & -1.341(21) \\
H_{\eta} & 0.0^c & 0.0^e & 0.0^e & 0.0^e & 0.0^e \\
H_{\xi} & 2.6(6) & 3.50_{(19)} & 5.85(34) & 940(37) & 1.79(40) \\
h_{\xi} & 0.0^e & 0.0^e & 0.0^e & 0.0^e & 0.0^e \\
h_{\zeta} & 3.2(3) & 3.01_{(26)} & 3.01^d & 3.013^d & 3.01^d \\
10^4 T_{\phi} & 1.7(1) & 1.933_{(81)} & 1.933^d & 1.933^d & 1.933^d \\
T_{\phi} & 986.11220(2) & 700.77379(2) & 455.77838(2) & 0.00024 & 0.00028 & 0.00028 \\
\end{array}
\]

\(a\)Values converted from Ref. 16, using \(c = 2.99792458 \times 10^{16}\) cm\(^{-1}\). 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 \(v_{\nu_1}, v_{\nu_4}\), and \(v_{\nu_1}\) 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\(^{13}\)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\(^{35}\)Cl (in cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Ground State</th>
<th>Microwave Data(^a)</th>
<th>Combined Data(^b)</th>
<th>3(^s) State</th>
<th>4(^t) State</th>
<th>5(^t) State</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.9014578(4)</td>
<td>1.940145886(43)</td>
<td>1.90187165(55)</td>
<td>1.8902375(11)</td>
<td>1.9098813(15)</td>
</tr>
<tr>
<td>B</td>
<td>0.19876576(5)</td>
<td>0.198765837(42)</td>
<td>0.199097849(87)</td>
<td>0.197879729(76)</td>
<td>0.19826451(10)</td>
</tr>
<tr>
<td>C</td>
<td>0.17971478(5)</td>
<td>0.179714845(39)</td>
<td>0.179384121(84)</td>
<td>0.178837023(73)</td>
<td>0.17910734(10)</td>
</tr>
</tbody>
</table>

#### Rotational constants

- \(10^4 \Delta_\alpha = 3.6345(60)\)
- \(10^5 \Delta_\alpha = -8.4149(53)\)
- \(10^5 \Delta_\beta = 1.093(2)\)
- \(10^6 \Delta_\delta = 6.4001(70)\)
- \(10^6 \delta_H = 1.4161(1)\)
- \(10^9 H_H = 3.2(5)\)
- \(10^{10} H_{H_{-δ}} = -1.427(34)\)
- \(H_{\text{m}} = 0.0^d\)
- \(H_{I_4} = 2.6(6)\)
- \(b_{\text{m}} = 3.3(3)\)
- \(b_{\text{t}} = 1.7(1)\)

#### Centrifugal distortion constants

- \(T_s = 986.07007(2)\)

\(^a\)Values converted from Ref. 16, using \(c = 2.99792458 \times 10^6\) cm\(^{-1}\). 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 \(v_4, v_9\), and \(v_9\) 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\(^{-1}\).

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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 \(v_4\) 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 \(ΔK_a ≠ 0\). From Table II, the only possibility for the perturbing level is \(v_6\), 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 \(ΔK_a = ± 2\). In a molecule of \(C_s\) symmetry, levels of \(a^t\) symmetry, such as \(v_6\), can interact with levels of \(a^t\) symmetry, such as \(v_4\), through \(a^t\) or \(b^t\)-axis Coriolis coupling...
Fig. 6. Systematic shifts in the higher \( K_a \) rotational levels of the \( 4^1 \) state of DCO\(^{15}\)Cl caused by a \( \Delta K_a = \pm 2 \) interaction with the \( \nu_4 \) 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 \( \nu_4 \), 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.

ACKNOWLEDGMENTS

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