Far-Infrared Laser Magnetic Resonance Detection of CH₂Cl

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Z. Naturforsch. 47a, 660 - 664 (1992); received February 6, 1992

New Far Infrared Laser Magnetic Resonance (LMR) spectra have been detected in the reaction of Cl atoms with CH₂CO. Based on chemical and kinetic evidence they were assigned to CH₂Cl radicals. The assignment was substantiated by subsequent experiments which employed the reactions of F atoms with CH₂Cl and Na atoms with CH₂Cl₂, respectively. The three different sources yielded identical spectra.

**Key words:** Laser Magnetic resonance, Radicals, Rotational spectroscopy.

1. Introduction

The chloromethyl radical, CH₂Cl, is a molecule of considerable interest in atmospheric as well as environmental chemistry. Cl substituted methyl radicals play a major role in the incineration of chlorine containing wastes [1-3]. Furthermore, CH₂Cl appears as a reactive chlorine carrier in the atmosphere, arising from oceanic emission of CH₃Cl and subsequent reaction with OH radicals [4]. However, despite its importance, as yet very little is known quantitatively about this important species.

The first spectroscopic investigations were performed with CH₂Cl trapped in argon matrices [5, 6]. The results confirmed a planar structure. Subsequently, ionization potentials were derived from photoelectron spectroscopy [7] and electron impact mass spectroscopy [8]. Rotational constants were determined by microwave spectroscopy [9]. Only few elementary reactions have been studied in detail so far [10-13], and little is known also concerning possible formation of CH₂Cl in a variety of potential source reactions.

In our laboratory, an investigation has recently been carried out [14] of the kinetics of the reaction

\[ \text{Cl} + \text{CH}_2\text{CO} \rightarrow \text{products}. \]

The study had employed the discharge-flow technique with mass spectrometric detection. Mass spectra were observed which pointed to both CH₂Cl as well as HCCO as major reaction products. These results on two interesting species have stimulated us to begin a search for spectra of either radical using Far-Infrared Laser Magnetic Resonance (FIR-LMR) detection [15], which in the past has enabled direct, specific, and highly sensitive observations of a large number of other small gas phase free radicals. Indeed, Radford has recently succeeded in detecting LMR spectra of the HCCO radical [16] generated in the reaction \( \text{O} + \text{C}_2\text{H}_2 \). Thus, a further investigation of the products of reaction (1) by LMR seemed in order.

In this communication, we report on some of the results that were obtained, namely the detection of a series of new LMR spectra which, based on chemical and kinetic evidence, could be attributed to the CH₂Cl radical.

2. Experimental

The experimental set-up consisted of a flow reactor coupled to an FIR-LMR spectrometer. A detailed description has been given elsewhere [17]. Briefly, an optically pumped FIR laser, which operated at a large number of molecular laser lines in the region 40 \( \mu \text{m} \leq \lambda \leq 1300 \mu\text{m} \), served as radiation source. The intra-cavity LMR sampling region was defined by the intersection of the FIR laser beam waist with the flow tube and the homogeneous region of the magnetic field. The field was modulated at a frequency of 5 kHz with a pair of Helmholtz coils. LMR signals were monitored with a liquid helium cooled InSb hot electron bolometer and, after phase sensitive detection with a lock-in amplifier, stored in a microcomputer, which also controlled the field scans.

For producing the radicals, Cl and F atoms in He carrier gas were generated in a microwave discharge...
in a quartz probe and admixed to the main flow tube. Gas phase Na atoms were produced by letting He flow over metallic Na in a stainless steel oven which was heated to temperatures in the range $570 \, \text{K} \leq T \leq 640 \, \text{K}$. The gas stream was introduced into the main flow tube via a heatable injector, which was held at a temperature $50^\circ \text{C}$ above that of the oven to avoid condensation. Reactions of the atomic species with the molecular radical precursors then occurred within a few milliseconds upstream of the LMR sampling region. The gas pressure was between 0.2 Torr $\leq p \leq 1$ Torr.

3. Results

The reaction of Cl atoms with CH$_2$CO

$$\text{Cl} + \text{CH}_2\text{CO} \rightarrow \text{products} \tag{1}$$
gave the first evidence for a new species detected with the LMR. Possible reaction channels of (1) are

\begin{align*}
\text{Cl} + \text{CH}_2\text{CO} & \rightarrow \text{CH}_2\text{Cl} + \text{CO}, \quad \Delta H_{298}^0 = -92 \, \text{kJ/mol}, \tag{1a} \\
& \rightarrow \text{HCCO} + \text{HCl}, \quad \Delta H_{298}^0 \approx 0 \, \text{kJ/mol}, \tag{1b} \\
& \rightarrow \text{HCO} + \text{CHCl}, \quad \Delta H_{298}^0 = +274 \, \text{kJ/mol}, \tag{1c} \\
& \rightarrow \text{CH}_3 + \text{CICO}, \quad \Delta H_{298}^0 = +280 \, \text{kJ/mol}. \tag{1d}
\end{align*}

Initial experiments were performed at an FIR laser wavelength of $\lambda = 373.6 \, \mu\text{m}$ (N$_2$H$_4$ laser gas pumped by the 10R 12 CO$_2$ laser line), which is a line where Radford had detected HCCO from the O + C$_2$H$_2$ reaction [16]. The 373.6 $\mu$m spectrum which we obtained from Cl + CH$_2$CO is displayed in Figure 1. It can be seen to consist of relatively complicated and broad patterns with only partially resolved structure and few narrow single lines. This is not unexpected for a non-linear asymmetric top molecule.

However, at 373.6 $\mu$m the HCCO radical had been found to exhibit an LMR spectrum with distinctive series of sharp lines and well resolved doublet hyperfine splittings [16]. Although a full analysis is not yet available, based on different pieces of chemical evidence and some tentative assignments based on the available microwave data [18] for HCCO, the identity of HCCO as the carrier of the spectra observed by Radford seems to be established on firm grounds [19].

In the present work, strong spectra of HCCO were readily detected in the O + C$_2$H$_2$ system. Completely identical spectra were obtained from the reaction F + CH$_2$CO $\rightarrow$ HF + HCCO. This confirms the conclusions by Radford. However, the spectra in Figure 1 are clearly entirely different from those of HCCO. Indeed, no signals of HCCO could be observed from reaction (1) even after varying the chemical conditions over a wide range (see discussion). Hence, HCCO (reaction 1) can easily be ruled out as the carrier of the new spectra.

Instead, product channels (1a) and (1c–d) must be considered. Of these, (1c) and (1d) are highly endothermic and cannot contribute at room temperature. However, CHCl could also arise from a consecutive reaction, namely

$$\text{CH}_2\text{Cl} + \text{Cl} \rightarrow \text{CHCl} + \text{HCl}, \quad \Delta H_{298}^0 = -11 \, \text{kJ/mol}. \tag{2}$$

In its electronic ground state CHCl is a singlet molecule ($\tilde{X}^1\text{A}^\text{a}$) which cannot be detected by LMR, but the origin of the first triplet state ($\tilde{A}^3\text{B}^\text{a}$) is at only $\Delta H_{298}^0 = 27 \, \text{kJ/mol}$ [20]. Formation of triplet CHCl in reaction (2) would thus be endothermic by 16 kJ/mol. Furthermore, any CHCl (â) should be rapidly deactivated in collisions with the bath gas (see below), so that CHCl is highly unlikely to be the species of interest.

Therefore, the CH$_2$Cl radical remains as the final plausible candidate molecule. CH$_2$Cl is strongly dipolar, and it should therefore have reasonably strong absorptions due to rotational transitions throughout the FIR regime.

The tentative assignment can be confirmed on chemical grounds by employing two other reaction systems. First, the reaction (see, e.g., [21])

$$\text{F} + \text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl} + \text{HF}, \quad \Delta H_{298}^0 = -157 \, \text{kJ/mol} \tag{3}$$

was studied. The 373.6 $\mu$m spectrum that was observed with this source reaction is shown in Figure 1. The spectrum is identical and of comparable intensity to that of the one from Cl + CH$_2$CO, supporting the proposed assignment to CH$_2$Cl. However, a subsequent reaction of CH$_2$Cl with F could lead to CHCl,

$$\text{F} + \text{CH}_2\text{Cl} \rightarrow \text{CHCl} + \text{HF}, \quad \Delta H_{298}^0 = -149 \, \text{kJ/mol}. \tag{4}$$

Reaction (4) is exothermic enough to generate CHCl in its lowest lying triplet state, thereby obscuring the assignment. The influence of CHCl could be ruled out by simulating reactions (3) and (4) as well as CH$_2$Cl + CH$_2$Cl, CH$_2$Cl + CHCl, CHCl + CHCl, and corresponding wall reactions of the radicals. Under the
Fig. 1. LMR spectrum at $\lambda = 373.6 \, \mu \text{m}$ with $\pi$ polarization obtained using the reactions Cl + CH$_2$CO, F + CH$_3$Cl, and Na + CH$_2$Cl$_2$. The measured spectra can be seen to be identical and are thus attributed to the CH$_2$Cl radical.

Table 1. FIR laser lines used to observe LMR spectra of CH$_2$Cl.

<table>
<thead>
<tr>
<th>Lasing gas</th>
<th>CO$_2$-Laser pump line</th>
<th>Laser wavelength ((\mu\text{m}))</th>
<th>Laser frequency (^a) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$H$_4$</td>
<td>10R24</td>
<td>301.275</td>
<td>995 077.8</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>9P12</td>
<td>331.699</td>
<td>903 889.4</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>10R12</td>
<td>373.577</td>
<td>802 492.8(^b)</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>9P14</td>
<td>416.522</td>
<td>719 751.2</td>
</tr>
<tr>
<td>HCOOH</td>
<td>9R22</td>
<td>418.613</td>
<td>716 156.8</td>
</tr>
<tr>
<td>HCOOH</td>
<td>9R20</td>
<td>432.667(^e)</td>
<td>692 951.4(^d)</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>10P24</td>
<td>435.772</td>
<td>687 957.4</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>10P16</td>
<td>461.07</td>
<td>650 207.7</td>
</tr>
<tr>
<td>HCOOH</td>
<td>9R28</td>
<td>513.002(^d)</td>
<td>584 388.2(^d)</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>10R28</td>
<td>533.678</td>
<td>561 747.5</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>9P16</td>
<td>570.567</td>
<td>525 427.5</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>9P24</td>
<td>614.284</td>
<td>488 034.7</td>
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<tr>
<td>HCOOH</td>
<td>9P24</td>
<td>694.189</td>
<td>431 859.8</td>
</tr>
<tr>
<td>HCOOH</td>
<td>9R24</td>
<td>742.572</td>
<td>403 721.7</td>
</tr>
<tr>
<td>HCOOH</td>
<td>9R24</td>
<td>744.050</td>
<td>402 919.6</td>
</tr>
</tbody>
</table>

\(^a\) References for laser frequencies may be found in [23].
\(^b\) Ref. [16].
\(^c\) A second laser line of the same gas and CO$_2$ pump line at $\lambda = 432.631 \, \mu \text{m}$ (692 895.0 MHz) has been reported. Both lines could not be distinguished with the present apparatus.
\(^d\) A second laser line of the same gas and CO$_2$ pump line at $\lambda = 513.016 \, \mu \text{m}$ (584 372.9 MHz) has been reported. Both lines could not be distinguished with the present apparatus.

Fig. 2. LMR spectra of CH$_2$Cl at $\lambda = 744.1 \, \mu \text{m}$ (a) and 461.1 \(\mu \text{m}\) (b) obtained with the reaction F + CH$_3$Cl.
Results of these ongoing investigations will be reported elsewhere.

As shown in Fig. 1, the observed spectra using reaction (6) were less intense, but they were clearly identical to those from the former two reaction systems. Hence, the assignment to CH₂Cl seems firmly established.

Since the F + CH₃Cl system provided the best control over the experimental conditions, subsequent searches for further spectra of CH₂Cl were performed with this source. In total, spectra were detected at 15 wavelengths between 301 µm ≤ λ ≤ 744 µm. Table 1 gives an overview. In nearly all cases, the spectra consisted of complicated broad patterns with only partially resolvable structure, sometimes combined with a few single signals with lower linewidths. Some examples are shown in Figure 2.

4. Discussion

Considering the chemical and kinetic evidence, the assignment of CH₂Cl as the carrier of the observed new 373.6 µm spectrum and of at least the majority of the other spectra that were detected seems to be unambiguous. However, a full spectroscopic analysis remains to be carried out. Endo et al. have obtained detailed molecular parameters of CH₂Cl from microwave spectra [9]. The radical has C₂ᵥ symmetry, its electronic ground state is 2B₁, and the unpaired electron is localized in a π π*-orbital. The rotational constants are A = 9.15, B = 0.53, and C = 0.50 cm⁻¹, i.e. the radical is an almost perfect prolate symmetric top. The present LMR spectra of CH₂Cl are thought to arise from a-dipole transitions (∆Kₘ = 0) between relatively high rotational states, e.g. N'' = 20 for the strongest spectrum at λ = 461.1 µm. However, while the microwave data should provide a starting point for a more detailed assignment, a full analysis is severely hampered by the complex and unresolved appearance of the spectra. Although attempts to resolve some of the observed signals by using lower pressure and small modulation fields were partially successful, they added to rather than resolved the problem. Complications arise due to the two Cl isotopes, ³⁵Cl and ³⁷Cl. Furthermore, because of the two H nuclei with total nuclear spin of Iₜ = 1 or 0 and the Cl atom with Iₜ = 3/2, the spectra are expected to exhibit a complicated hyperfine structure. It is noted, last but not least, that the LMR spectrum of CH₂F [22], which is not unlike that of CH₂Cl in appearance, is also still awaiting analysis.

Experimental data on the gas phase kinetics of CH₂Cl elementary reactions are very sparse to date [10–13]. The successful detection of CH₂Cl by LMR greatly expands the potential for further studies of its reactions, many of which are important in atmospheric chemistry. For the strongest transition at λ = 461.1 µm, an estimation of the sensitivity from simulations of the F + CH₃Cl system indicated a detection limit at a signal-to-noise ratio of S/N = 1 of better than 5 × 10⁹/cm³, which seems very encouraging indeed for future research on CH₂Cl kinetics. Concerning the product distribution of reaction (1), further measurements of the yields of CH₂Cl as well as HCCO are in progress. The mass spectrometric results [14] had indicated comparable orders of magnitude for both species. In the present work HCCO could not be observed from reaction (1), which suggests CH₂Cl to be the major reaction product. However, the LMR detection sensitivity for HCCO, which has not yet been determined, could be lower than for CH₂Cl. On the other hand, complications could arise in the mass spectrometric work due to fragmentation of CH₂CO or of a possible CH₂ClCO* complex in the ion source. Using reaction (3) for calibration, one can readily determine absolute CH₂Cl concentrations. Results of these ongoing investigations will be reported elsewhere.
Acknowledgements

This work has been supported by the Fond der Chemie. Thanks are due to H. Radford for communicating his HCCO LMR spectra prior to publication and to T. J. Sears and P. B. Davies for discussions concerning the assignments.