Far-Infrared Laser Magnetic Resonance Detection of CH_2Cl

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New Far Infrared Laser Magnetic Resonance (LMR) spectra have been detected in the reaction of Cl atoms with CH_2CO. Based on chemical and kinetic evidence they were assigned to CH_2Cl radicals. The assignment was substantiated by subsequent experiments which employed the reactions of F atoms with CH_3Cl and Na atoms with CH_2Cl_2, respectively. The three different sources yielded identical spectra.

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

1. Introduction

The chloromethyl radical, CH_2Cl, 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, CH_2Cl appears as a reactive chlorine carrier in the atmosphere, arising from oceanic emission of CH_3Cl 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 CH_2Cl 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 CH_2Cl in a variety of potential source reactions.

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

$$Cl + CH_2CO \rightarrow \text{products.} \qquad (1)$$

The study had employed the discharge-flow technique with mass spectrometric detection. Mass spectra were observed which pointed to both CH_2Cl 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 $O + C_2H_2$. 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 CH_2Cl 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 µm $\leqq \lambda \leqq$ 1300 µm, served as radiation source. The intracavity 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

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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 $570\,K \leqq T \leqq 640\,K$. The gas stream was introduced into the main flow tube via a heatable injector, which was held at a temperature 50° above that of the oven to avoid condensation. Reactions of the atomic species with the molecular radical precursors then occured within a few milliseconds upstream of the LMR sampling region. The gas pressure was between $0.2\,Torr \leqq p \leqq 1\,Torr$.

3. Results

The reaction of Cl atoms with CH_2CO

$$Cl + CH_2CO \rightarrow \text{products} \qquad (1)$$

gave the first evidence for a new species detected with the LMR. Possible reaction channels of (1) are

$$Cl + CH_2CO$$

$$\rightarrow CH_2Cl + CO, \quad \Delta H^0_{R298} = -92\,kJ/mol, \qquad (1\,a)$$

$$\rightarrow HCCO + HCl, \quad \Delta H^0_{R298} \approx 0\,kJ/mol, \qquad (1\,b)$$

$$\rightarrow HCO + CHCl, \quad \Delta H^0_{R298} = +274\,kJ/mol, \qquad (1\,c)$$

$$\rightarrow CH_2 + ClCO, \quad \Delta H^0_{R298} = +280\,kJ/mol. \qquad (1\,d)$$

Initial experiments were performed at an FIR laser wavelength of $\lambda = 373.6\,\mu m$ (N_2H_4 laser gas pumped by the 10 R 12 CO_2 line), which is a line where Radford had detected HCCO from the $O + C_2H_2$ reaction [16]. The 373.6 μm spectrum which we obtained from $Cl + CH_2CO$ 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 μm 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 $O + C_2H_2$ system. Completely identical spectra were obtained from the reaction $F + CH_2CO \rightarrow HF + HCCO$. 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 b) can easily be ruled out as the carrier of the new spectra.

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

$$CH_2Cl + Cl \rightarrow CHCl + HCl, \quad \Delta H^0_{R298} = -11\,kJ/mol. \qquad (2)$$

In its electronic ground state CHCl is a singlet molecule ($\tilde{X}\,^1A'$) which cannot be detected by LMR, but the origin of the first triplet state ($\tilde{a}\,^3B'$) is at only $\Delta H^0_{ST} = 27\,kJ/mol$ [20]. Formation of triplet CHCl in reaction (2) would thus be endothermic by 16 kJ/mol. Furthermore, any CHCl ($\tilde{a}$) 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_2Cl radical remains as the final plausible candidate molecule. CH_2Cl 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])

$$F + CH_3Cl \rightarrow CH_2Cl + HF, \quad \Delta H^0_{R298} = -157\,kJ/mol \qquad (3)$$

was studied. The 373.6 μm spectrum that was observed with this source reaction is shown in Figure 1. The spectrum is identical and of comparable intensity to the one from $Cl + CH_2CO$, supporting the proposed assignment to CH_2Cl. However, a subsequent reaction of CH_2Cl with F could lead to CHCl,

$$F + CH_2Cl \rightarrow CHCl + HF, \quad \Delta H^0_{R298} = -149\,kJ/mol. \qquad (4)$$

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 $CH_2Cl + CH_2Cl$, $CH_2Cl + CHCl$, $CHCl + CHCl$, and corresponding wall reactions of the radicals. Under the

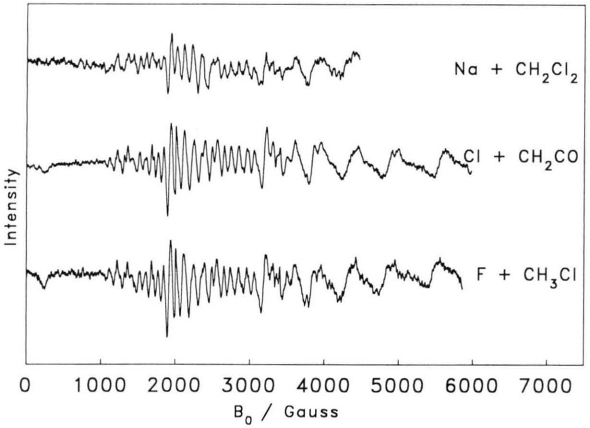

Fig. 1. LMR spectrum at $\lambda = 373.6$ µm with π polarization obtained using the reactions $Cl + CH_2CO$, $F + CH_3Cl$, and $Na + CH_2Cl_2$. The measured spectra can be seen to be identical and are thus attributed to the CH_2Cl radical.

Table 1. FIR laser lines used to observe LMR spectra of CH_2Cl.

Lasing gas	CO_2-Laser pump line	Laser wavelength (µm)	Laser frequency [a] (MHz)
N_2H_4	10R24	301.275	995 077.8
N_2H_4	9P12	331.699	903 889.4
N_2H_4	10R12	373.577	802 492.8 [b]
CH_3OH	9P14	416.522	719 751.2
HCOOH	9R22	418.613	716 156.8
HCOOH	9R20	432.667 [c]	692 951.4 [c]
N_2H_4	10P24	435.772	687 957.4
N_2H_4	10P16	461.07	650 207.7
HCOOH	9R28	513.002 [d]	584 388.2 [d]
N_2H_4	10R28	533.678	561 747.5
CH_3OH	9P16	570.567	525 427.5
CH_3OH	9P24	614.284	488 034.7
CH_3OH	9P24	694.189	431 859.8
HCOOH	9R40	742.572	403 721.7
HCOOH	9R24	744.050	402 919.6

[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 $\lambda = 432.631$ µm (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 $\lambda = 513.016$ µm (584 372.9 MHz) has been reported. Both lines could not be distinguished with the present apparatus.

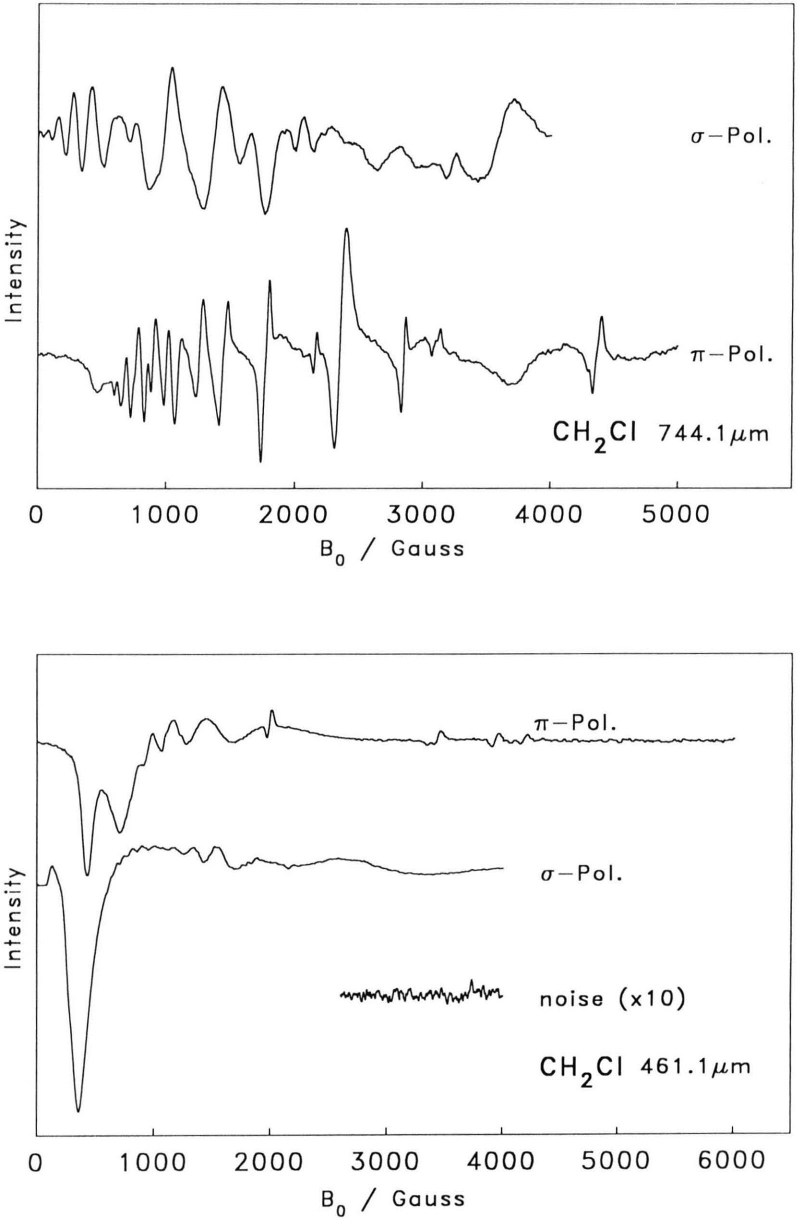

Fig. 2. LMR spectra of CH_2Cl at $\lambda = 744.1$ (a) and 461.1 µm (b) obtained with the reaction $F + CH_3Cl$.

experimental conditions the F atoms were consumed within a few hundred microseconds. As the total reaction time was about 3 ms, at least 2 ms were available for subsequent depletion reactions and triplet-singlet relaxation of CHCl. At the pressures used, this time interval should be sufficiently long to allow almost complete deactivation of the CHCl triplet state.

Last, for a final confirmation of CH_2Cl and exclusion of CHCl the reaction

$$Na + CH_2Cl_2 \rightarrow CH_2Cl + NaCl_{(g)}, \quad \Delta H^0_{R298} = -85\ \mathrm{kJ/mol} \tag{5}$$

was tested. In this case, the only possible consecutive reaction is

$$Na + CH_2Cl \rightarrow CH_2 + NaCl. \tag{6}$$

Formation of CHCl via

$$Na + CH_2Cl \rightarrow CHCl + NaH \tag{7}$$

would be endothermic by +220 kJ/mol.

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 CH_2Cl seems firmly established.

Since the $F + CH_3Cl$ system provided the best control over the experimental conditions, subsequent searches for further spectra of CH_2Cl were performed with this source. In total, spectra were detected at 15 wavelengths between $301\ \mu m \leqq \lambda \leqq 744\ \mu m$. 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 CH_2Cl 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 CH_2Cl from microwave spectra [9]. The radical has C_{2v} symmetry, its electronic ground state is $^2B_1$, and the unpaired electron is localized in a pπ-orbital. The rotational constants are $A = 9.15$, $B = 0.53$, and $C = 0.50\ \mathrm{cm}^{-1}$, i.e. the radical is an almost perfect prolate symmetric top. The present LMR spectra of CH_2Cl are thought to arise from a-dipole transitions ($\Delta K_a = 0$) between relatively high rotational states, e.g. $N'' = 20$ for the strongest spectrum at $\lambda = 461.1\ \mu m$. 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, ^{35}Cl and ^{37}Cl. Furthermore, because of the two H nuclei with total nuclear spin of $I_H = 1$ or 0 and the Cl atom with $I_{Cl} = 3/2$, the spectra are expected to exhibit a complicated hyperfine structure. It is noted, last but not least, that the LMR spectrum of CH_2F [22], which is not unlike that of CH_2Cl in appearance, is also still awaiting analysis.

Experimental data on the gas phase kinetics of CH_2Cl elementary reactions are very sparse to date [10–13]. The successful detection of CH_2Cl 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 $\lambda = 461.1\ \mu m$, an estimation of the sensitivity from simulations of the $F + CH_3Cl$ system indicated a detection limit at a signal-to-noise ratio of $S/N = 1$ of better than $5 \cdot 10^9/\mathrm{cm}^3$, which seems very encouraging indeed for future research on CH_2Cl kinetics. Concerning the product distribution of reaction (1), further measurements of the yields of CH_2Cl 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 CH_2Cl to be the major reaction product. However, the LMR detection sensitivity for HCCO, which has not yet been determined, could be lower than for CH_2Cl. On the other hand, complications could arise in the mass spectrometric work due to fragmentation of CH_2CO or of a possible CH_2ClCO^* complex in the ion source. Using reaction (3) for calibration, one can readily determine absolute CH_2Cl concentrations. Results of these ongoing investigations will be reported elsewhere.

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