Vibration-Rotation Spectrum of ClO and its Role in the Stratosphere

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ABSTRACT

The possible role in the stratosphere of vibrationally excited chlorine monoxide molecules in the ground electronic state is examined. An infrared vibration-rotation emission spectrum of chlorine monoxide is expected to arise following the neutral rearrangement reaction between atomic chlorine and ozone. The predicted vibration-rotation spectrum in the 676.75–4894.81 cm^{-1} region is described.

In recent years, studies on stratospheric chemistry have received increasing attention, partly because of concern that the emission from supersonic transports would undergo chemical reactions leading to a reduction in the concentration of stratospheric ozone. Such a reduction would permit more ultraviolet radiation to reach the lower atmosphere and consequently endanger life on earth's surface.

It is currently accepted that chlorine monoxide (ClO) is formed in the stratosphere by reaction of chlorine originating from the effects of the injection of odd chlorine into the ozonosphere. The input of chlorine into the atmosphere from fluorochloromethanes, mainly CF_2Cl_2 and $CFCl_3$, cause significant stratospheric O_3 depletion by means of the catalytic sequence chain reactions (Crutzen, 1974; Wofsy and McElroy, 1974; Stolarski and Cicerone, 1974; Molina and Rowland, 1974; Cicerone *et al.*, 1974):

$$Cl + O_3 \rightarrow ClO + O_2, \quad (1)$$

$$ClO + O \rightarrow Cl + O_2. \quad (2)$$

These reactions of neutral rearrangement processes are known to be very fast and exothermic. The main chain terminating reaction considered by the above investigators is the HCl forming reaction,

$$Cl + CH_4 \rightarrow HCl + CH_3. \quad (3)$$

The formation of perchloric acid, via the sequence of reactions

$$Cl + O_2 + O_3 \rightarrow ClO_3 + O_2, \quad (4)$$

$$ClO + OH \rightarrow HClO_4, \quad (5)$$

may be a more efficient sink than HCl for stratospheric chlorine (Simonaitis and Heicklen, 1975). Furthermore, the reactions of ClO with HO_2 and NO_2,

$$ClO + HO_2 \rightarrow HOCl + O_2, \quad (6)$$

$$NO_2 + ClO + M \rightarrow ClONO_2 + M, \quad (7)$$

possess the potential of significantly obstructing the completion of Cl–ClO–Cl cycle, at least in the region below 35 km (Prasad, 1976).

Some of the various complex problems associated with a proper understanding of stratospheric chlorine chemistry, which appear to be far more complex than what is implied in the current literature, are

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TABLE 1. Predicted vibration-rotation spectrum of chlorine monoxide.

Band v', v''	$^{35}Cl^{16}O$ $\Omega = 3/2$ Wavenumber (ν, cm^{-1})	$^{35}Cl^{16}O$ $\Omega = 1/2$ Wavenumber (ν, cm^{-1})	$^{37}Cl^{16}O$ $\Omega = 3/2$ Wavenumber (ν, cm^{-1})	$^{37}Cl^{16}O$ $\Omega = 1/2$ Wavenumber (ν, cm^{-1})
Δv = 1 sequence				
1, 0	843.96	841.70	836.86	834.62
2, 1	832.90	830.24	825.99	823.35
3, 2	821.68	818.62	814.97	811.94
4, 3	810.32	806.86	803.80	800.38
5, 4	798.81	794.94	792.50	788.67
6, 5	787.15	782.89	781.03	776.82
7, 6	775.33	770.67	769.43	764.82
8, 7	763.37	758.31	757.68	752.68
9, 8	751.26	745.81	745.78	740.39
10, 9	739.00	733.14	733.75	727.95
11, 10	726.60	720.34	721.55	715.38
12, 11	714.04	707.37	709.23	702.64
13, 12	701.33	694.27	696.74	689.78
14, 13	688.47	681.01	684.13	676.75
Δv = 2 sequence				
2, 0	1676.85	1671.94	1662.85	1657.97
3, 1	1654.58	1648.86	1640.96	1635.29
4, 2	1632.00	1625.48	1618.77	1612.32
5, 3	1609.13	1601.80	1596.30	1589.05
6, 4	1585.95	1577.83	1573.53	1565.49
7, 5	1562.48	1553.56	1550.46	1541.64
8, 6	1538.71	1528.98	1527.11	1517.50
9, 7	1514.64	1504.12	1503.46	1493.07
10, 8	1490.27	1478.95	1479.53	1468.34
11, 9	1465.60	1453.48	1455.30	1443.33
12, 10	1440.63	1427.71	1430.78	1418.02
13, 11	1415.37	1401.64	1405.97	1392.42
14, 12	1389.80	1375.28	1380.87	1366.53
Δv = 3 sequence				
3, 0	2498.54	2490.56	2477.82	2469.91
4, 1	2464.90	2455.72	2444.76	2435.67
5, 2	2430.81	2420.42	2411.27	2400.99
6, 3	2396.27	2384.69	2377.33	2365.87
7, 4	2361.28	2348.50	2342.96	2313.31
8, 5	2325.85	2311.87	2308.14	2294.32
9, 6	2289.97	2274.79	2272.89	2257.89
10, 7	2253.64	2237.26	2237.21	2221.02
11, 8	2216.86	2199.29	2201.08	2183.72
12, 9	2179.64	2160.85	2164.53	2145.97
13, 10	2141.96	2121.98	2127.52	2107.80
14, 11	2103.84	2082.65	2090.10	2069.17
Δv = 4 sequence				
4, 0	3308.85	3297.42	3281.62	3270.29
5, 1	3263.70	3250.66	3237.26	3224.34
6, 2	3217.95	3203.31	3192.30	3177.81
7, 3	3171.60	3155.36	3146.76	3130.69
8, 4	3124.66	3106.81	3100.64	3082.99
9, 5	3077.11	3057.68	3053.92	3034.71
10, 6	3028.97	3007.93	3006.64	2985.84
11, 7	2980.24	2957.60	2958.76	2936.40
12, 8	2930.90	2906.66	2910.31	2886.36
13, 9	2880.97	2855.12	2861.27	2835.75
14, 10	2830.43	2802.99	2811.65	2784.55

TABLE 1. (*Continued*)

Band v', v''	$^{35}Cl^{16}O$ $\Omega = 3/2$ Wavenumber (ν, cm^{-1})	$^{35}Cl^{16}O$ $\Omega = 1/2$ Wavenumber (ν, cm^{-1})	$^{37}Cl^{16}O$ $\Omega = 3/2$ Wavenumber (ν, cm^{-1})	$^{37}Cl^{16}O$ $\Omega = 1/2$ Wavenumber (ν, cm^{-1})
Δv = 5 sequence				
5, 0	4107.66	4092.36	4074.12	4058.96
6, 1	4050.85	4033.55	4018.29	4001.16
7, 2	3993.28	3973.98	3961.73	3942.63
8, 3	3934.98	3913.67	3904.44	3883.37
9, 4	3875.92	3852.62	3846.42	3823.38
10, 5	3816.12	3790.82	3787.67	3762.66
11, 6	3755.57	3728.27	3728.19	3701.22
12, 7	3694.27	3664.97	3667.99	3639.04
13, 8	3632.23	3600.93	3607.05	3576.14
14, 9	3569.44	3536.13	3545.40	3512.50
Δv = 6 sequence				
6, 0	4894.81	4875.25	4855.15	4835.78
7, 1	4826.18	4804.22	4787.72	4765.98
8, 2	4756.66	4732.29	4719.41	4695.31
9, 3	4686.24	4659.48	4650.22	4623.76
10, 4	4614.92	4585.76	4580.17	4551.33
11, 5	4542.71	4511.16	4509.22	4478.04
12, 6	4469.61	4435.64	4437.42	4403.86
13, 7	4395.60	4359.24	4364.73	4328.82
14, 8	4320.70	4281.94	4291.18	4252.89

discussed by Prasad (1976). The possible role of the vibrationally excited ClO molecules formed in reaction (1) has been emphasized by Prasad, who suggests that the production of ClO_3 via the reaction

$$ClO^* + O_2 + M \rightarrow ClO_3 + M, \qquad (8)$$

would be quite substantial in the stratosphere. Here the asterisk denotes the vibrationally excited state. The atmospheric implications of ClO_3 formation depends upon the frequency of ClO* production in reaction (1). This quantity depends jointly on the distribution of the vibrational quanta among the newly formed ClO molecules and the rate of collisional deactivation of ClO as a function of vibrational quantum number. Reaction (1) is analogous to the exothermic hydroxyl-producing process

$$H + O_3 \rightarrow OH^* + O_2 \qquad (9)$$

proposed by Bates and Nicolet (1950) and by Herzberg (1951), to explain the emission of the Meinel infrared bands in the airglow spectrum. On the basis of the experimental results of Charters *et al.* (1971) for the OH* production in reaction (9), a very high value approaching even 90% would be indicated for the frequency of the production of highly excited ClO* in reaction (1). However, it may be noted that the deposition of vibrational energy in a product depends on the shape of the potential energy surface along the reaction coordinate of the activated com-

plex. Since vibrational excitation can substantially effect the chemical behavior of species, the implications of ClO* formed in reaction (1) deserve careful investigation.

It may be thus possible that the exothermic reaction (1) will produce vibrationally excited ClO molecules in the ground state, from which an infrared vibration-rotation emission spectrum might be expected to arise, analogous to the Meinel OH airglow bands (Vallance-Jones, 1973). The infrared vibration-rotation spectrum of ClO is yet to be identified either in the laboratory or in the stratosphere. However, Nicholls (1975) has reported the predicted wavelengths of bands of the $\Delta v = 1, 2, 3, 4$ and 5 sequences of the vibration-rotation spectrum, in addition to the reinterpretation of the recently detected enhanced absorption at 3242 $\pm$ 2 Å in the Umkehr observations (Brewer *et al.*, 1972), based on the molecular constants of ClO ultraviolet system (Basco and Morse, 1973). In regard to these studies, it is worthwhile to note that the recent high-resolution studies of the ultraviolet bands of ClO by Coxon *et al.* (1976), provide revised molecular constants, which differ from those of the earlier studies. In view of the various atmospheric implications of ClO*, it seemed desirable to present the predicted wavelengths of the vibration-rotation spectrum, using the revised accurate molecular constants.

In Table 1 are presented the predicted band centers of the vibration-rotation bands for each substate of both the $^{35}Cl^{16}O$ and $^{37}Cl^{16}O$ molecules. It is seen that the bands of the $\Delta v = 1, 2, 3, 4, 5$ and 6 sequences are expected to lie in the 676.75–4894.81 cm^{-1} region. It is of interest to note the recent laboratory study of the ClO infrared absorption spectrum by Menzies *et al.* (1977). These authors have observed the ClO fundamental vibration-rotation band near 850 cm^{-1} using a tunable PbSnTe diode laser as a source of monochromatic radiation. They have reported the band centers for the $^{35}Cl^{16}O$ $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ subbands at 843.961 and 841.839 cm^{-1}, respectively, and $^{37}Cl^{16}O$ $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ subbands at 836.786 and 834.59 cm^{-1}, respectively. These bands' center positions are in good agreement with those reported in Table 1. An extension of these laboratory studies to the remaining sequences of the spectrum, together with the studies of the radiative lifetimes and the effects of quenching need immediate attention, in order that an attempt could be made to answer the various fundamental physico-chemical questions of stratospheric chlorine monoxide.

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