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Infrared and Raman Spectra of Chlorosulfonyl Isocyanate

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Chlorosulfonyl isocyanate, $\mathrm{ClSO_2NCO}$, was first prepared by Graf,[1] and the presence of –NCO and $>\mathrm{SO_2}$ groups in this compound was shown by Onodera[2] in his study of the infrared spectra of this compound. Detailed studies of the infrared and Raman spectra of this compound are of interest not only in themselves, but also in comparison with those of such related compounds with –NCO or $>\mathrm{SO_2}$ groups as sulfonyl diisocyanate, sulfuryl chloride, or sulfamide.

By using a liquid cell arranged so as to prevent the compound from hydrolysis, the infrared spectra were recorded in the NaCl region. The Raman spectra were observed photographically using Hg-e and -k lines for excitation. The polarization ratios were not determined, however. The frequencies of the infrared and Raman spectra are expected to be accurate to within ± 2 and ± 5 cm^{-1} respectively; their tentative assignments are listed in Table 1.

$\mathrm{ClSO_2NCO}$ may be formed by replacing a Cl atom of $\mathrm{SO_2Cl_2}$ with an NCO group; it belongs to the point group *Cs*, in which the plane containing the Cl–S–NCO group is perpendicular to that containing the $\mathrm{SO_2}$ group. Accordingly, the fifteen normal vibrations of this compound are reduced to $\Gamma = 10A' + 5A''$ and are active in both infrared and Raman spectra.

All the strong and medium Raman bands, except for two medium bands, one at 85 cm^{-1} which is present as the anti-Stokes line from Hg-k, and one at 1412 cm^{-1}, are assigned to A′ modes of vibration. A strong band at 130 cm^{-1} could be assigned to the bending vibration of the S–N=CO group, and the band at 85 cm^{-1} to the torsional virbation of this group. The S–N stretching frequency of this compound, 741 cm^{-1}, is lower than those of $\mathrm{SO_2(NH_2)_2}$,[3] 904 and 931 cm^{-1}. On the basis of these assignments, it is clear that the S–N=CO group does not have a linear form like $\mathrm{S^-{=}N^+{=}CO}$, but a bent form. By comparing the normal frequencies of $\mathrm{SO_2Cl_2}$,[4–10] $\mathrm{SO_2(NCO)_2}$,[11] and $\mathrm{SO_2(NH_2)_2}$[3] with those of $\mathrm{ClSO_2NCO}$, the assignments of the observed frequencies listed in Table 1 may be seen to be probable.

TABLE 1. THE ASSIGNMENT OF THE INFRARED AND RAMAN SPECTRA OF $\mathrm{ClSO_2NCO}$ (cm^{-1})

Infrared	Raman	Assignment
3590 m		2258+1353=3611
3230 vw		1412+1353+482=3247
2998 m		2258+741=2999
2823 vw		1412×2=2824
2704 w		1353×2=2706
2580 w		1412+1182=2594
2258 vs	2258 m(e)	N=C=O asym. str. A′
1998 w		1412+586=1998
1797 w		1182+623=1805
1496 w		1412+85=1497
1412 vs	1412 m(e,k)	$\mathrm{SO_2}$ asym. str. A″
1353 vs	1357 m(e,k)	N=C=O sym. str. A′
1218 w,sh		741+482=1223
1182 vs	1186 s(e,k)	$\mathrm{SO_2}$ sym. str. A′
1094 vw		482×2+132=1096
1060 vw		482+302+278=1062
989 vw		586+403=989
871 w		438+302+132=872
741 vs	744 s(e,k)	S–N str. A′
	632 vw(e,k)	N=C=O bend. A″
	586 s(e,k)	$\mathrm{SO_2}$ bend. A′
	482 s(e,k)	N=C=O bend. A′
	438 w(e,k)	$\mathrm{SO_2}$ rock. A″
	403 vs(e,k)	S–Cl str. A′
	302 m(e,k)	N-S-Cl bend. A′; $\mathrm{SO_2}$ twist. A″
	278 m(e,k)	$\mathrm{SO_2}$ wag. A′
	130 s(e,k)	S–N=CO bend. A′
	85 m(k+)	-NCO tors. A″.

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