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Force fields of carbonic dihalides

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Vibrational studies (including force field calculations) of carbonic dihalides-COX_2 (X = F, Cl, Br) have been reported by a number of workers (Hauswirth and Willner 1979 and references cited therein). However, the Potential Energy Distributions (PEDs) for the calculated frequencies are reported only for the $COBr_2$ molecule (Hauswirth and Willner 1979). The present note deals with the evaluation of PEDs using general valence force fields and a brief discussion of the assignments for the normal frequencies of COF_2, $COCl_2$ and $COBr_2$.

Internal and symmety coordinates and symmetrized force constants are identical to those given by earlier workers (Hauswirth and Willner 1979). The structural parameters for COF_2, $COCl_2$ and $COBr_2$ were taken from Mallinson *et al* (1975), Schneider and Stokr (1961) and Carpenter *et al* (1977) respectively. The computer program of Schachtschneider[+] was used to evaluate the G and F matrices and then the force fields (calculated frequencies, force constants and PEDs). An ICL-1904S computer has been used in the present case.

The force constants have been transferred from the work of Hauswirth and Willner (1979) and four (F_{11}, F_{12}, F_{13} and F_{45}-Hauswirth and Willner 1979) of the ten symmetrized force constants have to be kept constant during iteration. The observed frequencies and corresponding calculated frequencies alongwith their PEDs are given in Table 1.

A perusal of Table 1 shows that the assignments of the observed frequencies to the different normal modes of vibration for COF_2 by earlier workers are supported by PEDs and mixing of symmetry allowed normal modes with comparable magnitudes can be seen through PEDs.

For the $COBr_2$ molecule the PEDs' pattern for the calculated frequencies is similar to that of COF_2. However, due to the lower magnitudes of the $COBr_2$ stretching and BrCBr angle deformation modes the CO stretching mode uncouples from the CBr_2 symmetric stretching mode whereas the symmetric BrCBr angle deformation mode couples weakly with the CBr_2 symmetric stretching mode to

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Table I. Observed and calculated frequencies and PEDs* for COX_2 (X=F, Cl, Br).

X=		F			Cl				Br	
Species	Obs.	Cal.	PED	Obs.	Cal.	PED	Obs.	Cal.	PED§	PED†
a_1	1928	1928	94(1), 16(2) 8(3)	1827	1827	104(1), 6(2)	1828	1828	102 (1)	103(1)
	965	965	87(2), 7(1) 5(3)	567	567	99(2), 13(3)	425	425	100(2), 22(3)	90(2), 26(3)
	584	584	91(3)	297	297	90(3)	181	181	86(3), 4(2)	77(3), 11(2)
b_1	1249	1249	101(4), 30(5)	850	850	102(5), 48(4)	757	757	79(4), 65(5)	78(4). 65(5)
	626	626	78(5), 8(4)	440	440	67(4), 13(5)	350	350	46(5), 31(4)	45(5). 32(4)
b_2	774	774	100(6)	580	580	100(6)	512	512	100(6)	100(6)

*The numbers within brackets correspond to the force constants defined as $F_{11}=1$, $F_{22}=2$, $F_{33}=3$, $F_{44}=4$, $F_{55}=5$, $F_{66}=6$ and those outside the brackets to the contribution of the corresponding force constans. The force constants 1, 2, 3, 4, 5 and 6 correspond respectively to the C=O stretch CX_2 sym stretch, XCX sym. deformation, CX_2 anti-sym. stretch, XCX anti-sym. deformation and CO non-planar bend.

PEDs marked § are from present work and those with † from the work of Hauswirth and Willner (1979).

give rise to the frequency 181 cm^{-1}. Furthermore, the PED for the frequency 425 cm^{-1} shows that the mixing of the CBr_2 symmetric stretching with the symmetric BrCBr angle deformation mode is enhanced compared to the COF_2 case. Similar enhancements of the mixing of the respective modes with the other remaining modes can be seen in the PEDs for the frequencies 757 and 350 cm^{-1}.

For the $COCl_2$ molecule the pattern of PEDs for the fundamental frequencies under the a_1 species is intermediate to those for COF_2 and $COBr_2$. However, surprisingly enough for the b_1 frequencies of $COCl_2$ the pattern of PEDs is reversed compared to those for COF_2 and $COBr_2$. For COF_2 and $COBr_2$ the frequencies with higher magnitudes under the b_1 species contain larger contribution from antisymmetric CX_2(P=F, Br) stretching force constants whereas the frequency with the lower magnitude contains larger contribution from the antisymmetric XCX angle deformation mode. Contrary to this for $COCl_2$ the CCl_2 antisymmetric stretching force constant contributes more to the frequency 440 cm^{-1} and less to the frequency 850 cm^{-1} compared to the antisymmetric ClCCl angle deformation mode.

As far as the force constants are concerned, the earlier data (Hauswirth and Willner 1979) are more reliable as those are based on frequencies observed for more than one isotopic species.

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References

Carpenter J H, Smith J G, Thompson I and Whiffen D H 1977 *J. Chem. Soc. Faraday Trans.* 2 **73** 384

Hauswirth W and Willner H 1979 *Spectrochim. Acta* **35A** 271

Mallinson P D, McKean D C, Holloway J H and Oxton I A 1975 *Spectrochim. Acta* **31A** 143 and other references cited therein

Schneider B and Stokr J 1961 *Coll. Czec. Chem. Commun.* **26** 1221