ACTA CHEMICA SCANDINAVICA 20 (1966) 2611–2615

Spectroscopic Calculations on the Vibrations of Carbonyl Halides, Including the Coriolis Coefficients of Rotation-Vibration Interaction

K. V. RAJALAKSHMI* and S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The generalized mean-square amplitude quantities for carbonyl halides belonging to the planar XY_2Z molecular model have been calculated at 0° and 298°K. The Coriolis coupling coefficients of these molecules are also reported here.

In the present study the spectroscopic calculations of the generalized mean-square amplitudes of vibration and the Coriolis coupling coefficients have been carried out for COF_2, $COCl_2$, and $COBr_2$ on the basis of the L matrix reported by Overend and Scherer.[1]

MOLECULAR MODEL

The planar symmetrical XY_2Z molecules belong to the point group C_{2v} and possess 6 modes of vibration, which conventionally are assigned as

$$3A_1 + 2B_1 + B_2$$

They are all active in both infrared and Raman. The species designation corresponds to the choice of the y-axis perpendicular to the molecular plane (zx). This convention has presently been adopted when labelling the Coriolis coefficients. It should be mentioned, however, that this orientation does not conform the recommendations reported by Mulliken.[2] Following those recommendations, one should choose the x-axis as perpendicular to the molecule plane (yz). As a consequence the B_1 and B_2 species designations should be interchanged.

* Postdoctorate Research Fellow (1964). Present address: Department of Physics, Kerala University, c/o U.C.College, Alwaye, S. India.

SYMMETRY COORDINATES

It is desired to say some few words about the symmetry coordinates of the presently considered molecule model, although the particular set applied does not influence the physical quantities, as for instance the mean-square amplitudes.

Symmetry coordinates for planar symmetrical XY_2Z molecules have been given by several investigators,[1,3] and shall not be repeated here. We only wish to make one special point concerning the planar angle bendings. We have used the normalized combinations

$$2^{-\frac{1}{2}}(\beta_1 + \beta_2) \quad \text{and} \quad 2^{-\frac{1}{2}}(\beta_1 - \beta_2)$$

belonging to species A_1 and B_1, respectively. They are based on the symmetric equivalent set of the two YXZ bendings. Actually these bendings were multiplied by a constant factor with the dimension of length in our calculations, but that is immaterial for the point of the present discussion. Several investigators have used the three bendings α (YXY), β_1 and β_2 for producing the in-plane bending coordinates. Thus they introduced unnecessarily one redundant, which they later on removed by means of the condition

$$\alpha + \beta_1 + \beta_2 = 0$$

An account on this question has been given to some length by Cyvin.[4]

MEAN-SQUARE AMPLITUDE MATRIX

The mean-square amplitude matrix Σ is determined from the relation [5]

$$\Sigma = \mathrm{L}\ \delta\ \widetilde{\mathrm{L}}$$

where L is the normal-coordinate transformation matrix. δ represents the frequency parameters

$$\delta_k = (h/8\pi^2\ \nu_k)\ \coth(h\nu_k/2kT)$$

where h is Planck's constant, k is Boltzmann's constant, and T the absolute temperature. The vibrational frequencies (ν_k) of COF_2, $COCl_2$ and $COBr_2$ are given in Table 1; *cf.* Ref. 1.

Table 1. Vibrational frequencies (in cm^{-1}) for COF_2, $COCl_2$, and $CoBr_2$.

Species	Frequency	COF_2	$COCl_2$	$COBr_2$
A_1	ν_1	1928	1827	1828
	ν_2	965	567	425
	ν_3	584	285	181
B_1	ν_4	1249	849	757
	ν_5	628	440	350
B_2	ν_6	774	580	512

The generalized mean-square amplitudes of vibration, namely the mean-square parallel $\langle \Delta z^2 \rangle$, and perpendicular amplitudes $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$, and the mean cross product $\langle \Delta z\, \Delta x \rangle$ for COF_2, $COCl_2$, and $COBr_2$ at $T = 0$ and 298°K are listed in Table 2. These quantities are linear combinations of the mean-square amplitude matrix elements. $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ designate the in-plane and out-of-plane mean-square perpendicular amplitudes, respectively. The only nonvanishing mean cross products are in the present case those of the $\langle \Delta z\, \Delta x \rangle$ type as listed in Table 2.

Table 2. Generalized mean-square amplitudes (in Å²) for COF_2, $COCl_2$, and $COBr_2$. Vanishing quantities not listed.
X = F, Cl or Br.

$\langle \Delta z^2 \rangle$		COF_2	$COCl_2$	$COBr_2$
C—X	$T = 0$	0.001903	0.002410	0.002425
	298	0.001927	0.002642	0.002899
C=O	$T = 0$	0.001292	0.001349	0.001348
	298	0.001293	0.001351	0.001349
X···X	$T = 0$	0.002492	0.002967	0.002174
	298	0.002695	0.004772	0.005156
O···X	$T = 0$	0.002365	0.002668	0.002695
	298	0.002538	0.003217	0.003663
$\langle \Delta x^2 \rangle$		COF_2	$COCl_2$	$COBr_2$
C—X	$T = 0$	0.00205	0.002556	0.002573
	298	0.00219	0.003486	0.004164
C=O	$T = 0$	0.002609	0.003394	0.003810
	298	0.002817	0.003818	0.004470
X···X	$T = 0$	0.001354	0.000644	0.000195
	298	0.001518	0.000817	0.000283
O···X	$T = 0$	0.001524	0.002430	0.002862
	298	0.001685	0.003562	0.004988
$\langle \Delta y^2 \rangle$		COF_2	$COCl_2$	$COBr_2$
C—X	$T = 0$	0.002103	0.002392	0.002431
	298	0.002206	0.002702	0.002880
C=O	$T = 0$	0.002450	0.003622	0.004323
	298	0.002570	0.004092	0.005121
O···X	$T = 0$	0.000013	0.000127	0.000270
	298	0.000014	0.000144	0.000320
$\langle \Delta z\ \Delta x \rangle$		COF_2	$COCl_2$	$COBr_2$
C—X	$T = 0$	0.000086	0.000185	0.000186
	298	0.000086	0.000274	0.000336
O···X	$T = 0$	0.000248	0.000350	0.000500
	298	0.000307	0.000420	0.000738

MEAN AMPLITUDES OF VIBRATION

The mean amplitudes of vibration,

$$u = \langle \Delta z^2 \rangle^{\frac{1}{2}}$$

are known to be of great interest in gas electron-diffraction studies. The resulting calculated values for the considered carbonyl halides are given in Table 3.

Table 3. Mean amplitudes of vibration (in Å) for COF_2, $COCl_2$, and $COBr_2$. X = F, Cl or Br.

u		COF_2	$COCl_2$	$COBr_2$
C–X	$T = 0$	0.04363	0.04909	0.04925
	298	0.04390	0.05140	0.05385
C=O	$T = 0$	0.03594	0.03673	0.03671
	298	0.03596	0.03675	0.03673
X···X	$T = 0$	0.04992	0.05447	0.04662
	298	0.05192	0.06908	0.07181
O···X	$T = 0$	0.04863	0.05166	0.05191
	298	0.05038	0.05672	0.06052

CORIOLIS COUPLING COEFFICIENTS

The nonvanishing Coriolis coupling constants for the planar XY_2Z molecules arise from

$$A_1 \times B_1 = B_1, \qquad A_1 \times B_2 = B_2 \qquad \text{and} \qquad B_1 \times B_2 = A_2$$

The elements of the C^α matrices ($\alpha = x$, y, or z) are obtained by the vector method of Meal and Polo,[6] and the ζ^α values may be calculated according to the relation

$$\zeta^\alpha = L^{-1} C^\alpha \tilde{L}^{-1}$$

Table 4. Coriolis coupling coefficients in COF_2, $COCl_2$, and $COBr_2$.

	COF_2	$COCl_2$	$COBr_2$
ζ_{16}^x	0.291	0.305	0.273
ζ_{26}^x	−0.922	−0.936	−0.956
ζ_{36}^x	0.255	0.175	0.106
ζ_{14}^y	0.323	0.379	0.355
ζ_{24}^y	−0.770	−0.866	−0.915
ζ_{34}^y	0.550	0.327	0.189
ζ_{15}^y	0.044	0.367	0.644
ζ_{25}^y	0.593	0.465	0.386
ζ_{35}^y	0.804	0.805	0.660
ζ_{46}^z	−0.944	−0.983	−0.992
ζ_{56}^z	0.329	0.183	0.123

The values obtained for the Coriolis coupling coefficients of COF_2, $COCl_2$, and $COBr_2$ are listed in Table 4. They agree well with those reported by Oka and Morino.[7]

REFERENCES

1. Overend, J. and Scherer, J. R. *J. Chem. Phys.* **32** (1960) 1296.
2. Mulliken, R. S. *J. Chem. Phys.* **23** (1955) 1997.
3. Venkateswarlu, K., Thirugnanasambandam, P. and Balasubramanian, C. *Z. physik. Chem.* **218** (1961) 7; Venkateswarlu, K. and Rajalakshmi, K. V. *Acta Phys. Polon.* **22** (1962) 417.
4. Cyvin, S. J. *Acta Chem. Scand.* **20** (1966) 2616.
5. Cyvin, S. J. *Acta Polytechn. Scand.* (1960) Ph 6.
6. Meal, J. H. and Polo, S. R. *J. Chem. Phys.* **24** (1956) 1119.
7. Oka, T. and Morino, Y. *J. Mol. Spectry.* **11** (1963) 349.

Received June 15, 1966.