

VALENCE FORCE CONSTANTS, MEAN AMPLITUDES OF VIBRATION, AND  
THERMODYNAMIC FUNCTIONS OF CARBONYL SULPHIDE

BY G. SHANMUGASUNDARAM

Department of Chemistry, College of Engineering, Guindy, India\*

(Received November 13, 1968)

On the basis of the recent vibrational and structural data for carbonyl sulphide, four valence force constants as well as mean-square amplitudes of vibration and mean amplitudes of vibration at the room temperature have been computed by the symmetry considerations. In addition to these, molar thermodynamic functions, such as the enthalpy function, free enthalpy function, entropy, and heat capacity have also been computed for the temperature range 200–2000°K on the assumption of a rigid rotator, harmonic oscillator model. The results have been briefly discussed.

Carbonyl sulphide is a well-known and a simple triatomic molecule possessing a  $C_{2v}$  symmetry. Among the various spectroscopic investigations carried out for this molecule, the most recent one is the absorption spectrum in the region 1350–1420 Å investigated by Kopp [1] under high resolution followed by the vibrational analysis of the fundamental frequencies. Thus, the assigned fundamental frequencies for the molecule are given as follows:  $\nu_1(\Sigma^+) = 1324.9 \text{ cm}^{-1}$ ,  $\nu_2(\pi) = 469 \text{ cm}^{-1}$ , and  $\nu_3(\Sigma^+) = 723.5 \text{ cm}^{-1}$ . The frequencies  $\nu_1$  and  $\nu_3$  correspond to the  $C = O$  and  $C = S$  vibrations respectively and the frequency  $\nu_2$  corresponds to the  $O = C = S$  bending vibration. The frequency  $\nu_1$  and  $\nu_3$  are non-degenerate and parallel vibrations while  $\nu_2$  is the degenerate and perpendicular one. All the vibrations are allowed in both the infrared and Raman spectra [2]. The secular equations giving the normal frequencies in terms of the valence force constants were constructed with the help of the fundamental frequencies given above, and the molecular structural data [2] such as  $C = O = 1.16 \text{ Å}$  and  $C = S = 1.56 \text{ Å}$  by the Wilson group theoretical method [3]. Since it resulted to imaginary values for the off-diagonal element under the  $\Sigma^+$  species, the equations were solved in the manner described by Torkington [4]. The calculated values of the valence force constants in  $10^5 \text{ dynes/cm}$  are given as follows:  $f_r = 15.33$ ,  $f_R = 7.84$ ,  $f_{rR} = 1.76$  and  $f_\theta = 0.16$ . The force constant  $f_r$  due to  $C = O$  bond, and  $f_R$  due to  $C = S$  bond are well comparable with those of various polyatomic molecules [5] having similar chemical bonds. The stretching-stretching interaction force constant  $f_{rR}$

\* Address: Department of Chemistry, Clemson University, Clemson, South Carolina, USA.

is considerably high, and the bending force constant is considerably small, thereby establishing the fact that there is a strong coupling between the two stretchings. The positive sign obtained here for the interaction force constant is in line with the results of earlier investigators [6], [7]. According to Coulson, Duchesne and Manneback [6], the contribution of hybridisation between the  $s$  and  $p$  orbitals must give rise to a positive sign. According to Burnelle and Duchesne [7], if the configuration interaction is assumed, the excited states involved correspond to a contraction or expansion of both bonds simultaneously. On the other hand, if is contracted and the other bond is expanded, a positive sign results. Thus, the positive sign obtained here for the interaction constant is in line with the earlier studies [6], [7].

The secular equations giving the normal frequencies in terms of the mean square amplitude quantities were constructed at the room temperature with the help of the vibrational and structural data [1], [3]. The secular equations were solved in the same manner as done for the force constant calculations. The calculated values of the mean square amplitude quantities in  $\text{\AA}^2$  at the room temperature are given as follows:  $\sigma_r = 0.0012846$ ,  $\sigma_R = 0.0016798$ ,  $\sigma_{rR} = 0.0006584$  and  $\sigma_\theta = 0.0198603$ . The mean square amplitude quantity due to the  $C = S$  bond is greater than that of  $C = O$  bond. The quantity due to the bending of the molecule is very much greater than all other quantities. The arguments applicable to these quantities will be exactly reversed to those of valence force constants. The corresponding values of the mean amplitudes of vibration in  $\text{\AA}$  for the  $C = O$  and  $C = S$  bonds are 0.0359 and 0.041, respectively. The values of force constants and mean amplitudes of vibration presented here would be very useful in future for the evaluation of normal frequencies in other related molecules and for the interpretation of the results of electron diffraction studies.

The molar thermodynamic functions such as the enthalpy function, free enthalpy function, entropy, and heat capacity of carbonyl sulphide for the temperature range 200–2000°K were computed by using the fundamental frequencies in wave numbers and molecular structural data used for calculations of force constants and mean amplitudes of vibration. A rigid rotator, harmonic oscillator model was assumed and all the four thermodynamic functions were calculated for a gas in the thermodynamic standard gaseous state of unit fugacity. From the interbond distances, the rotational and translational contributions to the molarity, heat capacity, and free enthalpy functions for one mole of a perfect gas at a pressure of 1 atmosphere were obtained from the following expressions:

$$S_t^0 + S_r^0 = 2.2868 (7 \log T + 3 \log M + I_{xx} I_{yy} - 2 \log \sigma) - 6.6607$$

$$(C_p^0)_t + (C_p^0)_r = 7R/2 = 6.9552; H_t^0 + H_r^0 - H_0^0 = 7RT/2$$

where  $S_t^0$ ,  $S_r^0$ ,  $(C_p^0)_t$ ,  $(C_p^0)_r$ ,  $H_t^0$ ,  $H_r^0$ ,  $H_0^0$ ,  $R$  and  $T$  stand for entropy due to translation, entropy due to rotation, heat capacity due to translation, heat capacity due to rotation, enthalpy due to translation, enthalpy due to rotation, zero point energy, gas constant and absolute temperature.  $I_{xx}$  and  $I_{yy}$  are the principal moments of inertia along the  $x$  axis and  $y$  axis respectively.  $M$  is the molecular weight and  $\sigma$  is the symmetry number. The calculated

values of the principal moments of inertia for carbonyl sulphide are given as follows:

$$I_{xx} = I_{yy} = 830.1397 \text{ AMU } \text{\AA}^2 (1378.9699 \times 10^{-40} \text{ gcm}^2); I_{zz} = 0$$

The free enthalpy function due to translation and rotation was obtained by subtracting the heat capacities due to translation and rotation from the entropy contribution due to translation and rotation. The other standard formulae and tables of functions for the harmonic oscillator contributions given by Pitzer [8] were used. Assumed in the computation were a symmetry of 1, singlet ground state and chemical atomic weights. Neglected in the calculations were the contributions due to centrifugal distortion, isotopic mixing, nuclear spins and interactions between vibrations and rotations since the contributions of these to the total thermodynamic functions is negligibly small. The calculated values of all the four thermodynamic functions in calories per degree mole for carbonyl sulphide are given in Table I and they would be very useful in future for the interpretation of the experimental values of the same.

TABLE I

Enthalpy function, free enthalpy function, entropy, and heat capacity of carbonyl sulphide for the ideal gaseous state at a pressure of one atmosphere. (All the quantities are in cal. deg.<sup>-1</sup> mole<sup>-1</sup>)

$T(^{\circ}\text{K})$	$(H_0 - H_0^{\circ})/T$	$-(F_0 - H_0^{\circ})/T$	$S^{\circ}$	$C_p^{\circ}$
200	7.491	48.918	56.409	8.933
273.16	8.046	51.333	59.379	10.161
298.16	8.241	52.047	60.288	10.514
300	8.252	52.096	60.348	10.538
400	8.972	54.568	63.540	11.665
500	9.594	56.641	66.235	12.448
600	10.594	59.315	69.909	13.202
700	10.565	60.039	70.604	13.405
800	10.941	61.476	72.417	13.698
900	11.023	62.488	73.511	13.762
1000	11.540	63.994	75.534	14.085
1100	11.771	65.095	76.866	14.211
1200	11.976	66.122	78.098	14.310
1300	12.155	67.074	79.229	14.391
1400	12.327	68.007	80.334	14.460
1500	12.468	68.849	81.317	14.514
1600	12.598	69.665	82.263	14.559
1700	12.708	70.398	83.106	14.596
1800	12.822	71.184	84.006	14.628
1900	12.904	71.795	84.699	14.655
2000	12.998	72.486	85.484	14.679

The author is very much indebted to Professor. G. Nagarajan, Head of the Department of Physics, Allen University, Columbia, South Carolina, USA, for his valuable guidance and interest in this work.

## REFERENCE

- [1] I. Kopp, *Canad. J. Phys.*, **45**, 4011 (1967).
- [2] G. Herzberg, *Molecular spectra and Molecular structure II. Infrared and Raman spectra of polyatomic molecules*, D. Van Nostrand Company Inc, New York 1960.
- [3] H. J. Callomon and H. W. Thompson, *Proc. Roy. Soc.*, **222A**, 431 (1954).
- [4] P. Torkington, *J. Chem. Phys.*, **17**, 357 (1949).
- [5] L. Jensovsky, *Z. Chem.*, **12**, 453 (1963).
- [6] C. A. Coulson, J. Duchesne and Manneback, *V. Henri Mem. Vol.*, Desoer, Liege 1948, Page 33.
- [7] L. Burnelle and J. Duchesne, *J. Phys.*, **28**, 726 (1958).
- [8] K. S. Pitzer, *Quantum Chemistry*, Prentice-Hall, Inc., New York 1953.