Raman and InfraRed Spectra of Oxalyl Chloride

Joseph S. Ziomek, Forrest F. Cleveland, and Arnold G. Meister

---

Articles you may be interested in

---

tions of Fowler's argument, one finds

$$-W_2 = \pi\rho^2 \mathbb{Q} \left(\frac{1}{4} \int_0^h r^4 g(r) F(r) dr + \frac{2h}{3} \int_h^\infty r^3 g(r) F(r) dr \right.$$
$$\left. - \frac{h^2}{2} \int_h^\infty r^2 g(r) F(r) dr + \frac{h^4}{12} \int_h^\infty g(r) F(r) dr \right), \quad (2)$$

and

$$\partial(-W_2)/\partial h = \pi\rho^2 \mathbb{Q} \left(\frac{2}{3} \int_h^\infty r^3 g(r) F(r) dr \right.$$
$$\left. - h \int_h^\infty r^2 g(r) F(r) dr + \frac{h^3}{3} \int_h^\infty g(r) F(r) dr \right). \quad (3)$$

The type of detailed computation of W_3 used will depend on the nature of the adsorbent. For simplicity, we confine ourselves here to the following very approximate treatment: assume the adsorbent is structureless and that it does not perturb $g(r)$. Let the interaction energy between an adsorbent molecule and a liquid molecule be

$$u_1 = \epsilon_1 (r_1/r)^{12} - 2\epsilon_1 (r_1/r)^6. \quad (4)$$

Then the interaction energy between the entire adsorbent (density ρ_1) and a liquid molecule at a distance z from the plane adsorbent surface is[3]

$$\varphi = (\alpha/z)^9 - (\beta/z^3)$$
$$\alpha = \epsilon_1 r_1^{12} \pi \rho_1 / 45 \quad (5)$$
$$\beta = \epsilon_1 r_1^6 \pi \rho_1 / 3,$$

and the force is $-d\varphi/dz$. On integration, one finds the total interaction energy Φ between the liquid slab and the adsorbent (nearest edge of slab at distance z from adsorbent), and the corresponding total force f. Setting $d\Phi/dz = 0$ gives the equilibrium value of z, $z_0(h)$:

$$\alpha[(z_0+h)^{-9} - z_0^{-9}] = \beta[(z_0+h)^{-3} - z_0^{-3}]. \quad (6)$$

Then

$$W_3 = \int_{z_0}^\infty f dz$$
$$= \mathbb{Q}\rho \{ (\alpha/8)[z_0^{-8} - (z_0+h)^{-8}] - (\beta/2)[z_0^{-2} - (z_0+h)^{-2}] \}, \quad (7)$$

and

$$dW_3/dh = \mathbb{Q}\rho[\alpha(z_0+h)^{-9} - \beta(z_0+h)^{-3}]. \quad (8)$$

Substitution of Eqs. (3) and (8) into Eq. (1), using $N = \mathbb{Q}\rho h$, gives the adsorption isotherm. If we use

$$u(r) = \epsilon(r^*/r)^{12} - 2\epsilon(r^*/r)^6 \quad (9)$$

the isotherm reduces, for large $\Gamma = N/\mathbb{Q}$, to

$$\ln p/p_0 = (\delta - \delta_1)/\Gamma^3, \quad (10)$$
$$\delta = \pi\rho^4 \epsilon r^{*6}/3kT, \quad (11)$$
$$\delta_1 = \pi\rho^3 \rho_1 \epsilon_1 r_1^6/3kT. \quad (12)$$

Equation (10) is identical with Eq. (9) of reference 1, so we shall not discuss it further here.

[1] T. L. Hill, J. Chem. Phys. 17, 590 (1949).
[2] R. H. Fowler, Proc. Roy. Soc. A159, 229 (1937). See also J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 17, 338 (1949).
[3] T. L. Hill, J. Chem. Phys. 16, 181 (1948).

Raman and Infra-Red Spectra of Oxalyl Chloride

JOSEPH S. ZIOMEK*
Department of Chemistry,

AND

FORREST F. CLEVELAND AND ARNOLD G. MEISTER
Department of Physics, Illinois Institute of Technology, Chicago, Illinois
May 11, 1949

THE infra-red spectrum in the region 400–10000 cm^{-1} and the displacements, semiquantitative relative intensities, and depolarization factors of the Raman lines have been obtained

$\Delta\nu$	Raman I	ρ	Infra-red ν	I_ϵ
193	5	0.88		
261} 279}	33	0.37		
354	3	(0.96)		
443	21	0.51		
465	28	0.48		
483	30	0.50	488	S
522	7	P		
533	12	P	532	S
			594	S
620	100	0.17		
709	1	—		
			752	VVS**
802	VW	—		
			942	S
			1058	VVS
1081	5	0.32		
			1310	VS
			1388	S
1416	VW	—		
			1754	VVS
1781	57	0.79		
			1826	VVS
			2510	S
			2830	VS
			3740	VS
			5140	W

for liquid oxalyl chloride (ClOC–COCl) at room temperature. The depolarization factors were obtained by a previously described method[1] and the relative intensities were obtained with the aid of a Gaertner microdensitometer.[2] The infra-red absorption data were secured from records obtained with a Beckman IR-2 spectrophotometer with KBr optics. With a few exceptions, the present Raman data are in reasonably good agreement with the previous Raman data. So far as the authors have been able to determine, no previous infra-red data have been reported. The results are given in Table I.

An examination of the Raman and infra-red data indicates that there are only two coincident frequencies. Since in view of the large number of frequencies these two could well be chance coincidences, the rule of mutual exclusion may apply. If this is the case, the oxalyl chloride molecule has a center of symmetry and the structure would be that corresponding to the trans- or C_{2h} form. The values obtained for the depolarization factors and the absence of a second line near 1781 cm^{-1} in the Raman spectrum represents additional evidence for the trans-form. This evidence is in partial agreement with the conclusion reached by Martin and Partington[3] on the basis of dipole moment and molar refractivity measurements, namely, that the small dipole moment of 0.92 Debye unit could be explained by either free rotation or oscillation about the stable trans-position.

A normal coordinate treatment (FG matrix method) is being carried out for the trans- model in order to determine whether a satisfactory assignment of the observed frequencies can be made on the basis of this model. Further experimental details and the results of the normal coordinate treatment will be reported later.

* Present Address: Department of Chemistry, De Paul University, Chicago 14, Illinois.
[1] Forrest F. Cleveland, J. Chem. Phys. 13, 101 (1945).
[2] Forrest F. Cleveland, J. Chem. Phys. 11, 1, 227 (1943).
[3] G. T. O. Martin and J. R. Partington, J. Chem. Soc. 1178 (1936).