

RAMAN AND INFRARED SPECTRA OF PHENANTHRENEQUINONE

G. D. BARUAH, D. N. TRIPATHI AND S. NATH

Spectroscopy Department, Banaras Hindu University, Varanasi-5 (U.P.)

ABSTRACT

The Raman and infrared spectra of phenanthrenequinone have been studied in the region 250–4000 cm^{-1} . Vibrational assignments of all the prominent bands have been made by taking aid from the crystal spectrum of phenanthrene. A close correspondence has been observed between the fundamental vibrational frequencies of the molecules phenanthrene and phenanthrenequinone.

INTRODUCTION

THE vibrational spectra of several polycyclic aromatic hydrocarbons, e.g., naphthalene,¹ anthracene,²⁻⁸ pyrene,⁹ perylene,¹⁰ phenanthrene,¹¹ naphthoquinone,¹² anthraquinone¹² and several condensed ring aldehydes¹³ have been studied in detail at various laboratories. The spectra of these molecules are usually complex and the assignments are essentially based on the analysis of the crystal spectra. The interpretation of crystal spectra helps to a great extent the identification of the symmetry species of the observed bands. The present paper describes the result obtained for phenanthrenequinone including the analysis of the infrared spectra taken in nujol and KBr and Raman spectrum recorded with the help of Laser source. The crystal spectrum of phenanthrenequinone is not available at present. Thus the assignment has been made with the help of the crystal spectrum of phenanthrene¹¹ because of the structural similarity of the two molecules.

EXPERIMENTAL

The infrared spectrum of the molecule was measured between 4000–250 cm^{-1} with the aid of a Perkin-Elmer Grating Spectrophotometer (Model 521). The thin film spectra were recorded by making paste of compounds with nujol and pressed between two CsBr windows and also in KBr. Phenanthrenequinone used was reagent grade purified by sublimation. The laser traced Raman spectrum was obtained through the courtesy of Prof. J. R. Durig of South Carolina University.

RESULTS AND DISCUSSIONS

The molecule belongs to the point group C_{2v} . The 66 normal modes of vibration would be divided among the symmetry species $23 A_1 + 11 A_2 + 10 B_1 + 22 B_2$.

The molecule is assumed to be planar. The Z -axis is chosen as the highest symmetry axis (i.e., C_2 -axis) passing through the middle point of the CC bond between two C=O bonds. Out

of 66 normal modes of vibrations, 55 are infrared-active while 11 vibrations belonging to A_2 are inactive in infrared. All vibrations are Raman-active. The assignments of the bands have been made by taking aid from the vibrational assignment of the crystal spectrum of phenanthrene¹¹ and from the similar molecules. Table I collects the available data for phenanthrenequinone including the Raman spectrum and infrared spectra taken in nujol and KBr.

A₁ fundamentals.—It has been observed that the frequencies 750, 1035, 1160, 1230, 1420, 1504, 3015 and 3050 cm^{-1} appear with considerable intensity. These can be correlated with the frequencies 710, 1038, 1142, 1200, 1441, 1524, 3020 and 3050 cm^{-1} in the Raman spectrum of phenanthrene crystal identified as A_1 fundamentals. The ring-breathing frequency in the infrared spectrum has been observed at 760 cm^{-1} and in the Raman spectrum, this has been identified with frequency 750 cm^{-1} . In the crystal spectrum of phenanthrene the ring-breathing mode of vibration has been identified with a strong band at 710 cm^{-1} . A very strong band at 1679 cm^{-1} in the Raman spectrum and at 1675 cm^{-1} in the infrared spectrum of the molecule has been undoubtedly assigned to C=O stretching mode of vibration as this band appears very prominently in all other quinones¹² and have been assigned as A_1 fundamentals.

A₂ fundamentals.—The 11 fundamentals of A_2 species are infrared-inactive for a free molecule but may appear in the crystal spectrum. The Raman frequencies 360 and 468 cm^{-1} in phenanthrenequinone do not have any counterparts in the infrared spectrum. Thus these two can be conveniently chosen as fundamentals of A_2 type.

B₂ fundamentals.—A very strong band at 614 cm^{-1} in the Raman spectrum and at 620 cm^{-1} in the infrared spectrum has been assigned as the out-of-plane skeletal deformation of B_2

TABLE I
Vibrational assignments of phenanthrenequinone

Raman	I.R. nujol	I.R. KBr	Assignment	
352 (w)	310 (3)	308 (1)	B ₁ Skeletal deformation o.p.	
	360 (3)	356 (2)	A ₂ Skeletal deformation o.p.	
	370 (2)	368 (2)	B ₁ Skeletal deformation o.p.	
	380 (3)	380 (1)	B ₁ Skeletal deformation o.p.	
	395 (2)	385 (2)	A ₁ C=O bending i.p.	
	430 (3)	422 (6)	B ₁ Skeletal deformation o.p.	
468 (w)	526 (6)	510 (7)	B ₁ Skeletal deformation o.p.	
614 (s)	620 (4)	618 (3)	B ₁ Skeletal deformation o.p.	
	735 (5)	730 (2)	B ₁ Skeletal deformation o.p.	
750 (ms)	760 (7)	758 (6)	A ₁ Ring breathing	
	790 (1)	782 (5)	B ₁ C—H bending o.p.	
	840 (1)	835 (1)	A ₁ Skeletal deformation i.p.	
	870 (2)	879 (3)	B ₁ C—H bending o.p.	
	923 (2)	929 (3)	B ₁ C—H bending o.p.	
	960 (3)	965 (4)	B ₁ C—H bending o.p.	
	1016 (s)	1010 (2)	1012 (2)	B ₂ C—H bending i.p.
	1035 (w)	1035 (2)	1030 (4)	A ₁ C—H bending i.p.
1160 (s)	1120 (3)	1165 (2)	B ₂ C—H bending i.p.	
1230 (w)	1160 (3)	1225 (3)	A ₁ C—H bending i.p.	
1286 (vs)	1229 (4)	1284 (7)	B ₂ C—C stretching	
	1285 (10)	1292 (4)	A ₁ C—C stretching	
1355 (w)	1289 (6)	1330 (3)	A ₁ C—C stretching	
	1335 (3)	1365 (5)	B ₂ C—C stretching	
1420 (s)	1360 (6)	1420 (2)	A ₁ C—C stretching	
1504 (w)	1425 (6)	1571 (4)	B ₂ C—C stretching	
	1560 (3)	1600 (8)	B ₂ C—C stretching	
1593 (s)	1592 (7)	1660 (2)	A ₁ C—C stretching	
	1655 (2)	1680 (9)	B ₂ C—C stretching	
1679 (vs)	1675 (10)	2725 (1)	A ₁ C=O stretching	
	2720 (2)	2980 (2)	A ₁ 2724 = 1425 (A ₁) + 1299 (A ₁)	
	2981 (2)	3010 (2)	B ₂ 2985 = 1560 (B ₂) + 1425 (A ₁)	
	3015 (vw)	3050 (1)	B ₂ C—H stretching	
3050 (vw)	3020 (1)	3050 (1)	A ₁ C—H stretching	
	3050 (1)	3109 (1)	B ₂ C—H stretching	
	3115 (2)	3170 (5)	A ₁ 3152 = 1592 (A ₁) + 1560 (A ₁)	
	3150 (3)	3359 (2)	A ₁ C—H stretching	
	3188 (3)		A ₁ 3350 = 2 × 1675 (A ₁)	
	3350 (2)			

Intensities are given in the parenthesis.

s = strong; w = weak; vs = very strong; vw = very weak; sh = shoulder.

type and are correlated with the frequencies 618 and 614 cm.⁻¹ observed in the infrared and Raman spectra respectively of phenanthrene. Ten fundamentals are identified at 614, 1016, 1035, 1160, 1420, 1505, 1593, 3015 and 3050 cm.⁻¹ These can be very easily correlated with the frequencies 618, 1002, 1039, 1148, 1500, 1548, 3024 and 3064 cm.⁻¹ identified as B₂ fundamentals in the Raman spectrum of phenanthrene.

B₁ fundamentals.—The B₂ fundamentals are non-planar and they are readily identified by making comparison with the spectrum of phenanthrene. These fundamentals have weak Raman activity and they are generally assigned

from their characteristic *a*-polarisation. The bands occurring at 960, 870, 840, 735 and 430 cm.⁻¹ are B₁ fundamentals and can be identified with the frequencies 951, 874, 819, 735 and 431 cm.⁻¹ of phenanthrene.

Owing to the close similarity of the molecules, phenanthrene and phenanthrenequinone, some conclusions can be drawn from a comparison of their fundamental vibrations. It has been found that except for the carbonyl group vibrations there is a close correspondence between the fundamentals of the two molecules. Thus, the assignment in the present case as given in Table I is essentially correct.

ACKNOWLEDGEMENT

We wish to express our thanks to Prof. J. R. Durig for making available to us the Raman spectrum of the compound. One of us (G. D. B.) is thankful to the C.S.I.R. for the award of a Fellowship.

1. Sheerer, J., *J. Chem. Phys.*, 1962, **36**, 3308
2. Bruhn, W. and Mecke, R., *Z. Electrochem.*, 1961, **65**, 543.
3. Califano, S., *J. Chem. Phys.*, 1962, **36**, 903.
4. Colombo, L. and Mathieu, J., *Bull. Soc. Franc. Mineral Cryst.*, 1961, **83**, 250.
5. Califano, S., *Ris. Sci.*, 1963, **3**, 461.

6. Colombo, L., *Spectrochim. Acta*, 1964, **20**, 547.
7. Abasbegovic, N., Vukotic, N. and Colombo, L., *J. Chem. Phys.*, 1964, **41**, 2575.
8. Evans, D. J. and Scully, D. B., *Spectrochim. Acta*, 1964, **20**, 891.
9. Abbondanza, G. and Califano, S., *J. Chem. Phys.*, 1963, **39**, 1016.
10. Ambrosino, F. and Califano, S., *Spectrochim. Acta*, 1965, **21**, 1401.
11. Schettino, V., Neto, N. and Califano, S., *J. Chem. Phys.*, 1966, **44**, 2724.
12. Singh, S. N. and Singh, R. S., *Spectrochim. Acta*, 1968, **24 A**, 1591.
13. Singh, K., Singh, S. Nath and Rai, D. K., *Indian J. Pure & Appl. Phys.*, 1969, **7**, 638.

A NEW APPROACH TO ELOVICH EQUATION

R. P. VISWANATH, B. VISWANATHAN, V. SRINIVASAN AND M. V. C. SASTRI

Department of Chemistry, Indian Institute of Technology, Madras-36

THE chemisorption kinetic data are often analysed through a logarithmic relationship associated with Elovich.¹ Attempts²⁻⁴ have been constantly made to rationalise this empirical equation by the use of suitable models based on the presence of site distribution on the surface of the solid. The integrated expression of the Elovich equation has the form:

$$q = \frac{1}{\alpha} \ln(t + t_0) - \frac{1}{\alpha} \ln t_0$$

where q is the amount of gas adsorbed (in cc NTP) at any time t and α and t_0 are constants. Since t_0 is usually small, it is often neglected and the experimental kinetic data are often examined through a plot of q as a function of $\log t$, the slope of which yields the value of α and the intercept could be used to evaluate another constant of the Elovich equation, namely, ' a ', through the relationship $t_0 = 1/a\alpha$. The dependence of these constants on temperature and pressure, though studied widely,⁵ has not resulted in understanding the functional relationship of these parameters. In the present study, an attempt has been made to elucidate the physical significance of the parameters and to evolve methods for evaluating them from primary kinetic data on the chemisorption of hydrogen on iron oxide.

Iron oxide was prepared by the decomposition of AnalaR grade ferric nitrate in air at $400 \pm 10^\circ \text{C}$. for 9 hours. The results reported here pertain to adsorption by 3.13 gm. of the oxide (Fe_2O_3) whose surface area was found

to be 14.0 m^2 by the BET method. The measurements of adsorption were carried out in a volumetric apparatus similar to the one reported by Srinivasan.⁶ Each adsorption experiment was preceded by evacuation for an hour at the temperature of the experiment, to avoid reduction by previously adsorbed hydrogen, followed by evacuation at 400°C . for 8 hours at 10^{-6} mm. Hg .

The evaluation of t_0 .—Attempts to calculate q making use of the integrated equation have not resulted in getting values that were obtained experimentally, obviously on account of the omission of the constant t_0 in the plots of Elovich equation. In the present study a successive approximation procedure has been utilised to obtain the values of the integration constant t_0 . This was done by successively regressing the value of t_0 , obtained approximately from the intercept of the plot of q versus $\log t$ of the Elovich equation, till a self-consistent value for t_0 was reached.

The evaluation of ' a '.—A plot of the amount adsorbed as a function of time, with the condition that $q = 0$ at $t = t_0$, is made, and from the initial slope of this plot the value of ' a ', the initial rate, can be obtained.

The values of the parameters obtained by the treatment of experimental data on the adsorption of hydrogen on iron oxide in the temperature range $299-433^\circ \text{K}$., by the above procedure are summarised in Table I. Recently, McIntock⁷ has considered the parameters of