

Rhodopin (I) trimethylsilyl ether had the same absorption spectrum in visible light as I¹ and R_F -value = 0.75 (2 % acetone in petroleum ether) on circular kieselguhr paper,¹⁵ compared with R_F = 0.18 for I in the same system.

In a parallel experiment isozeaxanthin (III, 1.21 mg) was treated in like manner. The di-trimethylsilyl ether was obtained in quantitative yield, exhibited the same absorption spectrum in visible light as II and had R_F = 0.11 (petroleum ether) on kieselguhr paper, compared with R_F = 0.60 (10 % acetone in petroleum ether) for II.

Hydrolysis of rhodopin (I) trimethylsilyl ether to I. Treatment of I-trimethylsilyl ether in petroleum ether with excess of water by repeated shaking in a separatory funnel, resulted in a 3 % conversion to I as judged by spectrophotometric and paper-chromatographic examination.

Mechanical shaking for 1 h of the same mixture resulted in a 5 % hydrolysis to I. Shaking overnight in 30 % aqueous methanol resulted in no further hydrolysis.

Treatment of the trimethylsilyl ether with 10 % glacial acetic acid in ether overnight gave no significant hydrolysis, whereas alkaline hydrolysis in 5 % methanolic KOH-solution (followed paper-chromatographically) was completed after 22 h.

In parallel experiments hydrolysis of III-di-trimethylsilyl ether was tested. Treatment with water or methanol resulted in no significant hydrolysis. Only partial hydrolysis was achieved in 10 % glacial acetic acid in ether for 19 h. Alkaline hydrolysis in 5 % methanolic KOH-solution was completed in 1 h.

Acknowledgement. Rhodopin and 1,2,1',2'-tetrahydro-1,1'-dihydroxy-lycopen were kindly provided by Dr. J. D. Surmatis and isozeaxanthin by Dr. O. Isler, Hoffmann-La Roche & Co. Azafirin was a gift from Professor R. Kuhn, Heidelberg. One of us (SLJ) is grateful to *Norges tekniske hogskoles Fond* for a grant.

1. Liaaen Jensen, S. *Kgl. Norske Videnskab. Selskabs, Skrifter* **1962** No. 8.
2. Jackman, L. M. and Liaaen Jensen, S. *Acta Chem. Scand.* **15** (1961) 2058.
3. Ryvarden, L. and Liaaen Jensen, S. *Acta Chem. Scand.* **18** (1964) 643.
4. Surmatis, J. D. and Ofner, A. *J. Org. Chem.* **28** (1963) 2735.
5. Jackman, L. M. and Liaaen Jensen, S. *Acta Chem. Scand.* **18** (1964) 1403.

6. Liaaen Jensen, S., Hegge, E. and Jackman, L. M. *Acta Chem. Scand.* **18** (1964) 1703.
7. Hertzberg, S. and Liaaen Jensen, S. *Acta Chem. Scand.* **20** (1966) 1187.
8. Friedman, S. and Kaufman, M. L. *Anal. Chem.* **38** (1966) 144.
9. Sweeley, C. C., Bentley, R., Makita, M. and Wells, W. W. *J. Am. Chem. Soc.* **85** (1963) 2497.
10. Golding, B. T., Rickards, R. W. and Barber, M. *Tetrahedron Letters* **37** (1964) 2615.
11. Hedgley, E. J. and Overend, W. G. *Chem. Ind. (London)* **1960** 378.
12. Langer, S. H., Friedel, R. A., Wender, I. and Sharkey, A. G. *Anal. Chem.* **30** (1959) 1353.
13. Schwieter, U., Bollinger, H. R., Chopard-dit-Jean, L. H., Englert, G., Kofler, M., König, A., Planta, C. v., Rüegg, R., Vetter, W. and Isler, O. *Chimia* **19** (1965) 294.
14. Kuhn, R., Winterstein, A. and Roth, H. *Ber.* **64** (1931) 338.
15. Jensen, A. and Liaaen Jensen, S. *Acta Chem. Scand.* **13** (1959) 1863.

Received July 8, 1966.

Spectroscopic Studies on Metal Carbonyls

V. Mean Amplitudes of Vibration and Shrinkage Effects for Nickel Tetracarbonyl

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

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

The previous papers of this series^{1,2} are concerned with hexacarbonyls of octahedral symmetry. In one of them² the calculated mean amplitudes of vibration and Bastiansen-Morino shrinkage effects for chromium and molybdenum hexacarbonyls are reported. The studies on

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

metal carbonyls have got renewed actuality by the recently reported electron-diffraction work³ on iron pentacarbonyl with trigonal bipyramidal symmetry. It is planned to undertake the spectroscopic calculations of mean amplitudes of vibration and shrinkage effects for that compound too; in the interim we wish to give a short communication of some results on nickel tetracarbonyl, already completed in 1964.

Table 1. Mean amplitudes of vibration (Å units) for nickel tetracarbonyl. For discussion of the values in parentheses, see the text.

Distance	$T = 0$		298 °K	
	Ni—C	0.0472 (0.0481)	0.0522 (0.0537)	
C—O	0.0348 (0.0345)	0.0349 (0.0345)		
Ni...O	0.0481 (0.0492)	0.0538 (0.0555)		
C...C	0.0805 (0.0819)	0.1320 (0.1397)		
C...O	0.0891 (0.0913)	0.1621 (0.1730)		
O...O	0.1057 (0.1095)	0.2177 (0.2342)		

Table 2. Bastiansen-Morino shrinkage effects (Å units) for nickel tetracarbonyl.

Distance	$T = 0$		298 °K	
	Ni...O	0.0057 (0.0060)	0.0073 (0.0080)	
C...C	0.0024 (0.0028)	0.0080 (0.0101)		
C...O	0.0078 (0.0083)	0.0170 (0.0201)		
O...O	0.0125 (0.0134)	0.0272 (0.0320)		

Nickel tetracarbonyl, Ni(CO)₄, is known to have tetrahedral symmetry. The present calculations are primarily based on the normal-coordinate matrix (L) from Murata and Kawai.⁴ The matrix was used to establish a force field, which reproduces accurately the vibrational frequencies quoted by the same authors.⁴ Tables 1 and 2 show the results obtained for the mean amplitudes of vibration and Bastiansen-Morino shrinkage effects, respectively. The latter quantities are all derived from the bonded mean distances, say r_g (Ni—C) and d_g (C—O). In accordance, one has for instance for the nonbonded O...O distance:

$$-\delta = r_g' - \frac{1}{2} 6\frac{1}{2} (r_g + d_g)$$

where r_g' is the mean distance of O...O. The calculated shrinkage effect for the nonbonded C...O distance is the "practical" shrinkage in the terminology of Mornio, Cyvin, Kuchitsu and Iijima.⁵

It was found desirable to investigate the effect of a slightly changed assignment of frequencies due to Pistorius,⁶ and mainly based on the work of Jones.⁷ Hence a new force field was produced to fit accurately the frequencies from the mentioned source,⁶ keeping the L matrix from our previous calculation unchanged. The resulting mean amplitudes of vibration and Bastiansen-Morino shrinkage effects are included in parentheses in Tables 1 and 2. They are seen to display hardly significant differences, which probably would fall within the error limits of an electron-diffraction experiment.

The mean amplitude of vibration for the Ni...O distance may seem surprisingly small, being of practically the same magnitude as the bonded Ni—C amplitude. The same observation was made for the other metal carbonyls investigated.²

The study of metal carbonyls is particularly attractive due to high symmetries of the appropriate molecule models. By the same reason they provide excellent examples of nonlinear shrinkage effects with cancelling anharmonic terms. Also in the trigonal bipyramidal pentacarbonyls the shrinkage of any nonlinear conformation is of the same type.

1. Brunvoll, J. and Cyvin, S. J. *Acta Chem. Scand.* **18** (1964) 1417; Cyvin, S. J. and Brunvoll, J. *Acta Chem. Scand.* **18** (1964) 1023, 1423.
2. Brunvoll, J. *J. Mol. Spectry.* **15** (1965) 386.
3. Davis, M. I. and Hanson, H. P. *J. Phys. Chem.* **69** (1965) 3405.
4. Murata, H. and Kawai, K. *J. Chem. Phys.* **26** (1957) 1355; Kawai, K. and Murata, H. *J. Chem. Soc. Japan* **78** (1957) 494.
5. Morino, Y., Cyvin, S. J., Kuchitsu, K. and Iijima, T. *J. Chem. Phys.* **36** (1962) 1109.
6. Pistorius, C. W. F. T. *Spectrochim. Acta* **15** (1959) 717.
7. Jones, L. H. *J. Chem. Phys.* **23** (1955) 2448.

Received June 15, 1966.