dienes, is strongly predisposed to the concerted 1,4 mechanism;[5] **1t** (2.7% 1,2 addition) and **1c** (6.0% 1,2 addition) are both intermediate in their behavior toward cyclopentadiene between ethylene (no 1,2 addition) and 1,1-dichloro-2,2-difluoroethylene, which yields 16.6% of the 1,2 adduct.[3]

Acknowledgment. R. W. thanks the National Science Foundation for a Graduate Fellowship from 1966 to the present. This research was supported by grants from the National Science Foundation and the National Institutes of Health.

Robert Wheland, Paul D. Bartlett
Converse Memorial Laboratory, Harvard University
Cambridge, Massachusetts 02138

Received March 3, 1970

Excitation Profiles of Laser Raman Spectra in the Resonance Region of Two Carotenoid Pigments in Solution

Sir:

Using the emissions at the frequencies available from the argon-ion laser, we have obtained the excitation profiles of resonance-enhanced Raman spectra,[1–16] well within the lowest optical absorption band, of two carotenoid pigments[17–19] in solution. These profiles differ substantially from the absorption spectrum and therefore contain new information concerning the electronic structure of the pigment molecules. Although one expects the resonance-enhanced Raman effect (RRE) to be quite a general phenomenon, its applicability to the study of electronic structures of molecules still hinges on the availability of suitable excitation sources in the shorter wavelengths. The extreme sensitivity attainable by the RRE makes it a potentially powerful analytical tool.[5,15] In particular, it has been applied to detect spectra of pigments in live tissue.[20] The experiment amounts to measuring the intensities of the Raman lines[3,15] as a function of the excitation frequency, as the latter is swept through the regions of electronic absorption (excitation profile, EP).[14] Before the advent of lasers, most of these experiments were carried out indirectly (using one or two excitation frequencies and shifting the absorption spectrum by changing temperature or molecules in a homologous series).[3,21–23] The eight emissions from an A-ion laser allowed the direct acquisition of EP data of all-*trans* β-carotene and lycopene[17–19] with much finer grain than in the experiments cited above.

In addition to the two Raman lines reported in the past for β-carotene[4,24,25] at $\bar{\nu}_1$ 1158 and $\bar{\nu}_2$ 1527 cm^{-1}, assigned, respectively, to single- and double-bond stretching modes of the conjugated chain,[26,27] we have observed a number of additional transitions in the region of fundamental vibrations; the shoulder on the $\bar{\nu}_1$ transition was resolved into three sharp transitions at 1215, 1193, and 1176, $\bar{\nu}_4$ = 1006, and $\bar{\nu}_5$ = 961 cm^{-1}. The strongest overtones were found at $\sim 2\bar{\nu}_1 = 2313$, $\sim \bar{\nu}_1 + \bar{\nu}_2 = 2679$, $\sim \bar{\nu}_1 + \bar{\nu}_4 = 2163$, and $\sim 2\bar{\nu}_2 = 3048$. The spectrum of lycopene was quite similar, with $\bar{\nu}_1 = 1158$ and $\bar{\nu}_2 = 1515$ cm^{-1}. Figure 1 shows examples of the Raman spectra. Vibrational assignments are not discussed here.

As an internal standard of intensity we used the lines of the *n*-hexane solvent, which does not absorb in the visible and has Raman lines within 100 cm^{-1} (in most cases within 50 cm^{-1}) of the carotenoid lines; this separation is sufficiently small so that differential absorption corrections[15] can be neglected—this was checked by carefully studying the location of the lines within the absorption spectrum of the pigments. The $\bar{\nu}^4_{\text{Raman}}$ correction[15] was also found to be negligible. As a measure of intensity, we take ratios of the areas of the pigment and the adjacent hexane lines. The relative intensity factors thus obtained for a fixed sample at variable excitation frequencies represent the excitation profile. The EP's for fundamentals were taken in very dilute solutions ($c \lesssim 1\ \mu M$) using a transmission setup.[28] The more concentrated samples, used to study the overtones, were examined by a reflection technique.[28] The samples were repeatedly checked for chemical stability by remeasuring the fundamental Raman lines and the optical absorption spectrum (using a Cary 14).

In Figure 2 we plotted the excitation profiles for various Raman lines of the two pigments studied and compared them to the corresponding absorption spectra.

In both cases, the longest wavelength of excitation exceeds that of the first absorption peak. Nevertheless, enhancement is already appreciable—as evidenced by the observability of the lines at 10^{-7} *M* concentrations.

In β-carotene we see two well-defined intensity peaks: the peak at λ ∼476 nm in the EP of the fundamentals is quite close to the lowest absorption peak, being, however, much sharper than the latter; the peak in the EP of the overtones occurs at λ ∼467 and is distinct

---

(1) M. Harrand, *C. R. Acad. Sci.*, **226**, 241 (1948).

(2) P. P. Shorygin, *Dokl. Akad. Nauk SSSR*, **87**, 201 (1952).

(3) J. Behringer and J. Brandmüller, *Z. Elektrochem.*, **60**, 643 (1956).

(4) J. Behringer, *ibid.*, **62**, 544 (1958).

(5) J. Brandmüller, *Z. Anal. Chem.*, **170**, 29 (1959).

(6) L. N. Ovander, *Opt. Spektrosk.*, **4**, 556 (1958).

(7) W. Maier and F. Dörr, *Appl. Spectrosc.*, **14**, 1 (1960).

(8) A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960).

(9) D. G. Rea, *J. Mol. Spectrosc.*, **4**, 499 (1960).

(10) H. W. Schrötter, *Z. Elektrochem.*, **64**, 853 (1960).

(11) L. L. Krushinskii and P. P. Shorygin, *Opt. Spectrosc.*, **11**, 12, 80 (1961).

(12) A. C. Jones and D. D. Tunnicliff, *Anal. Chem.*, **34**, 261R (1962).

(13) P. P. Shorygin, *Pure Appl. Chem.*, **4**, 87 (1962).

(14) V. A. Zubov in "Physical Optics," Proceedings of the Lebedev Physics Institute, Academy of Science, USSR, Vol. 30, D. V. Shobel'tsyn, Ed., English Translation, Consultants Bureau, New York, N. Y., 1966.

(15) J. Behringer in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 6.

(16) R. C. C. Leite, T. C. Damen, and J. F. Scott in "Spectra of Solids," Proceedings of the International Conference on Light Scattering, Sept 1968, G. B. Wright, Ed., Springer-Verlag, Heidelberg, p 359.

(17) P. Karrer and E. Jucker, "Carotenoids," Elsevier, Amsterdam, 1950.

(18) L. Zechmeister, "Cis-Trans Isomeric Carotenoids, Vitamins A and Arylpolyenes," Academic Press, New York, N. Y., and Springer-Verlag, Vienna, 1962.

(19) T. W. Goodwin, Ed., "Chemistry and Biochemistry of Plant Pigments," Academic Press, New York, N. Y., 1965.

(20) D. Gill, R. G. Kilponen, and L. Rimai, *Nature (London)*, in press.

(21) M. Y. Tsenter and Ya. S. Bobovich, *Opt. Spectrosc.*, **16**, 134, 228 (1964).

(22) P. P. Shorygin and T. M. Ivanova, *Dokl. Akad. Nauk SSSR*, **150**, 533 (1963); *Sov. Phys. Dokl.*, **8**, 493 (1963).

(23) T. M. Ivanova, L. A. Yanovskaya and P. P. Shorygin, *Opt. Spectrosc.*, **18**, 1115 (1965).

(24) J. Behringer and J. Brandmüller, *Ann. Phys.*, **4**, 234 (1959).

(25) H. Jonaitis, *Liet. Fiz. Rinkinys*, **3**, 439 (1963).

(26) E. M. Popov and G. A. Kogan, *Opt. Spectrosc.*, **17**, 362 (1964).

(27) C. Tric, *J. Chem. Phys.*, **51**, 4778 (1969).

(28) P. J. Hendra and P. M. Stratton, *Chem. Rev.*, **69**, 325 (1969).

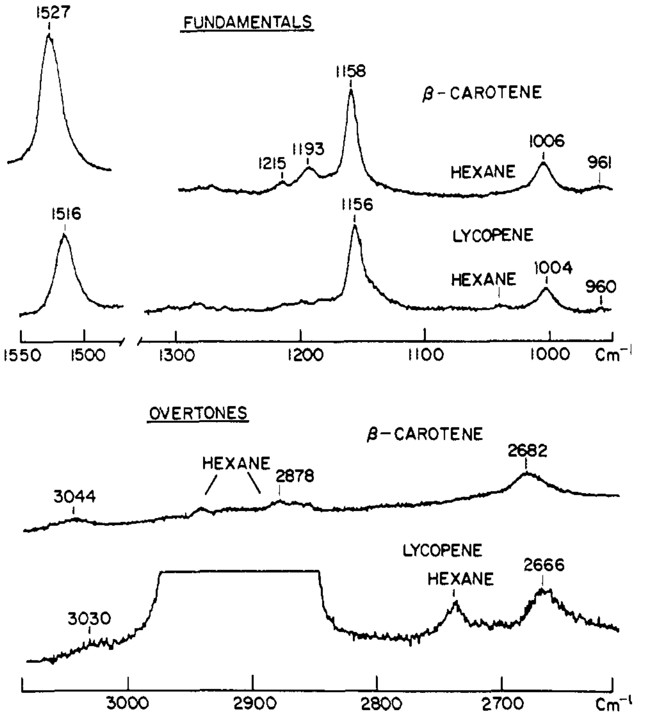

Figure 1. Example of resonance-enhanced Raman (RR) spectra of carotenoid solutions in *n*-hexane taken in a reflection geometry: [β-carotene] 100, [lyocpene] 4.5 μM; argon laser excitation at 488 nm for β-carotene and 514.5 nm for lycopene; laser power ~100 mW; incident and analyzed scattered *E* field perpendicular to scattering plane; Jarrell-Ash 75-cm Czerny-Turner double grating monochromator, photon counting digital detector; integration time ~1 sec; scanning rate 20 cm^{-1}/min.

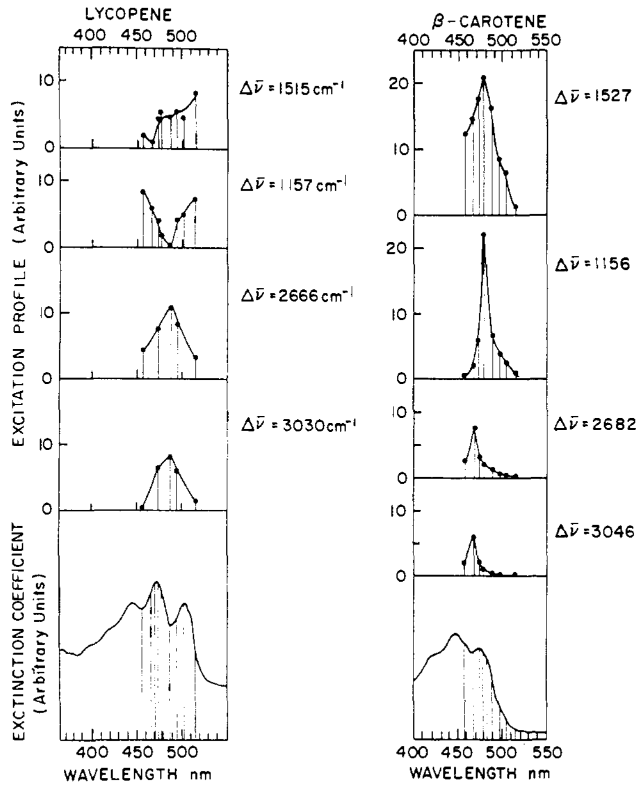

Figure 2. Excitation profiles of several fundamental and overtone lines in the RR spectra of β-carotene and lycopene in *n*-hexane solutions. Solvent Raman lines were used as internal standards. Vertical lines emphasize the eight monochromatic emissions of the argon laser used for excitation. Fundamentals at $\Delta\bar{\nu} < 1600$ cm^{-1}; the rest are overtones. Corresponding sections of the absorption spectra are shown at the lower part.

from any of the absorption peaks. In lycopene, we observe a peak at $\lambda \sim 490$ in the overtone EP, and the slope of the fundamental EP indicates the presence of a peak at a wavelength much longer than the first absorption peak.

In lycopene, we have a clear indication that the frequency of the 0–0 transition $\bar{\nu}_{00}$ is lower than that of the lowest electronic absorption peak at $\bar{\nu}$ 19,802 cm^{-1} (λ 505 nm), since the slope of the excitation profile for Raman fundamentals shows the presence of at least one peak below this frequency. Such may also be the case of β-carotene and of many other polyenes.[29] Although the vibrational fundamentals are very similar in both our samples, the vibronic splittings in the absorption spectra are different. If we assume that the vibrational frequencies in the excited state are close to those of the ground state,[27] we conclude that whereas in β-carotene the vibronic splitting (1240-cm^{-1} separation between the first two absorption maxima) corresponds to ν_1, in lycopene it is ν_2 (1566-cm^{-1} separations between absorption peaks). If, by analogy, we further assume that in carotene the $\bar{\nu}_{00} + n\bar{\nu}_1$ states contribute to the EP of the Raman fundamentals and the $\bar{\nu}_{00} + m\bar{\nu}_2$ states contribute to the EP of overtones (with the reverse perhaps true for lycopene), we can assign the difference between the two peaks of the two EP's of β-carotene to $(2\bar{\nu}_1 - \bar{\nu}_2) \simeq 740$ cm^{-1}, thus predicting for the excited state $\bar{\nu}_2 \sim 1500$ cm^{-1}. Such a scheme would also predict two more EP peaks, at $\bar{\nu}_{00}$ and at $\bar{\nu}_{00} + 1120$, both within the range of our experiments, and which we have not observed. This, however, could be expected, since generally different vibronic sublevels in the excited state are expected to contribute differently to the EP.[10,30-32]

Acknowledgment. We acknowledge helpful discussions with Mrs. M. H. Heyde and Mr. J. L. Parsons.

---

(29) A. J. Thompson, *J. Chem. Phys.*, **51**, 4106 (1969).

(30) P. P. Shorygin, *Zh. Fiz. Khim.*, **25**, 341 (1951).

(31) A. Kh. Khalilov, *ibid.*, **26**, 612 (1952).

(32) L. L. Krushinskii and P. P. Shorygin, *Sov. Phys. Dokl.*, **6**, 54 (1961).

L. Rimai, R. G. Kilponen, D. Gill
Scientific Research Staff
Ford Motor Company, Dearborn, Michigan 48121

Received March 10, 1970

Mechanistic Aspects of the Reaction of Acids with Some Platinum–Acetylene Complexes

Sir:

The oxidative addition reaction of a number of protonic acids to low-valent platinum complexes has been studied by a number of workers.[1-4] We have

---

(1) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

(2) D. M. Roundhill, *ibid.*, **9**, 254 (1970).

(3) D. Morelli, A. Segre, R. Ugo, G. La Monica, S. Cenini, and F. Conti, *Chem. Commun.*, 524 (1967).

(4) I. Harvie and R. D. W. Kemmitt, *ibid.*, 198 (1970). The unusual reaction of $(PPh_3)_4Pt$ with aldehydes described in this publication gives complexes of stoichiometry $Pt(COEt)_2(PPh_3)_2$ and $Pt(COPh_3)_2(PPh_3)_2$. The reported infrared spectra of these complexes are identical, however, with $Pt(COOEt)_2(PPh_3)_2$ and $Pt(COOPh)_2(PPh_3)_2$ prepared from $Pt(CO_3)(PPh_3)_2$ and the corresponding acids, and it is very likely that the reported complexes are the dicarboxylates rather than the diacyls.