

For a full discussion of the anisotropic rotation diffusion model and the fit results obtained therewith, reference is made to the previous paper.⁴ In Table IX only $(\Delta J)_{av}$ values have been listed, the first two columns relating to fits of the PMA methyl relaxation data (using eq 7-9), the last column to fits of the methylene data (using eq 10-12). As explained in ref 4, the methylene relaxation in the anisotropic rotation-diffusion model involves separate relaxation rates for each of the deuterons. In the fit procedure these rates were combined to a single rate using the experimental conditions of the actual relaxation measurement. An analogous procedure is not possible for the spectral densities. Accordingly, in stead of the $(\Delta J)_{av}$ values, $(\Delta R)_{av}$ values are given which are defined relative to the relaxation rates in an analogous way as $(\Delta J)_{av}$ to the spectral densities. In general $(\Delta R)_{av}$ values have been found to be very similar to the corresponding $(\Delta J)_{av}$ values. In the analysis in terms of the rotation diffusion model the emphasis has been put on simultaneous fitting of the methyl and methylene relaxation data. The accuracies of these fits are given in columns 2 and 3. As an illustration also $(\Delta J)_{av}$ values from separate fitting of the methyl data only are listed in column 1. In Figures 5 and 6 the dotted lines correspond to rotation diffusion fits to methyl samples at $\alpha' = 0.0$ and $\alpha' = 1.0$, respectively.

Coming now to a final comparison of the various models investigated, it appears that as to goodness of fit the simultaneous rotation diffusion fits to the methylene data give results which are very similar to the three-Lorentzian fits. For the methyl data the simultaneous rotation diffusion fits are somewhat less good

than the three-Lorentzian fits, but better than the corresponding model-free results (using the three-Lorentzian description of the overall motion). In order to properly assess the fitting power of a particular model the goodness of fit should be considered in relation with the number of parameters.

Giving marginally better fit accuracies, the three-Lorentzian analysis involves by far the largest number of parameters, i.e., 10 (taking the methyl and methylene fits together). Even if one assumes that the methyl and the methylene data could be fitted with the same set of correlation times without damaging too much the goodness of fit, the simultaneous three-Lorentzian fits still would involve seven independent parameters. This figure must be compared with seven for the (three-Lorentzian) model-free analysis and six for the simultaneous rotation diffusion analysis.

It is therefore concluded that taking into account both the goodness of fit and the number of independent parameters the rotation diffusion description shows the best overall ability to cope simultaneously with the present methyl and methylene relaxation data. Although of course it is clear that the rotation diffusion description has the additional advantage of easy physical interpretability of the fit parameters, it is interesting to note that in spite of the different nature of the instantly considered models a number of very similar physical observations could be made, in particular relating to the internal motion characterizing the methyl relaxation.

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Studies of Resonance Raman Scattering: High-Pressure Effects in β -Carotene

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The first measurements of the effect of pressure on the resonance Raman excitation profile of a molecule are reported. The measurements on β -carotene were done at 70 kbar and 298 K in a diamond anvil cell in a pentane-isopentane solution. At this pressure the absorption spectrum is red shifted about 3000 cm^{-1} . The excitation profiles for ν_1 and ν_2 have been measured. The data have been analyzed with a multimode model. It is concluded that, although pressure produces a very large shift in the absorption, no significant changes in the linear coupling parameters are observed.

Introduction

The study of the effects of high pressure on the electronic states of organic and biochemical molecules has a long history. The experimental studies and theoretical models up to this time have been concerned mainly with effect of pressure on the absorption and luminescence spectra. We have previously studied the effect of pressure on the absorption spectra of β -carotene¹ as well as the effect of temperature on the resonance Raman excitation profile of this same molecule.² In this paper, we will extend these studies by presenting the results of the effect of pressure on the resonance Raman excitation profiles of the two strongest Raman modes of β -carotene.

Pressure produces several effects³⁻⁵ in molecular electronic spectra. These are (1) a pressure dependence of the absorption and luminescence peak positions and (2) a broadening of these peaks. There is usually a shift toward lower energies ("red" shift) with the position being described by both linear and quadratic terms in the pressure. The shift tends to saturate at high pressure. A general broadening of the absorption and luminescence bands is also observed.

In order to explain these data, several theoretical models have been proposed. Since most of the experiments are done with the molecule of interest in solution, various theories of solvent effects on absorption have been used. The dielectric theories of Bayliss⁶ and McRae⁷ are most notable in being applied to explain the red shift of the electronic absorption spectra with pressure. These solvent theories do not explain the broadening or the quadratic pressure dependence that is observed.

A class of models using the ideas of configurational coordinates was initially proposed by Drickamer, Frank, and Slichter^{8,9} (DFS).

(1) Z. Z. Ho, T. A. Moore, S. H. Lin, and R. C. Hanson, *J. Chem. Phys.*, **74**, 873 (1981).

(2) Z. Z. Ho, R. C. Hanson, and S. H. Lin, *J. Chem. Phys.*, **77**, 3414 (1982).

(3) H. W. Offen in "Organic Molecular Photophysics", J. B. Birks, Ed., Wiley, London, 1973.

(4) B. Y. Okamoto and H. G. Drickamer, *J. Chem. Phys.*, **61**, 2870 (1974).

(5) L. A. Brey, G. B. Schuster, and H. G. Drickamer, *J. Chem. Phys.*, **71**, 2765 (1979).

(6) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

(7) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

(8) H. G. Drickamer, C. W. Frank, and C. P. Slichter, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 933 (1972).

(9) N. G. Drickamer and C. W. Frank, "Electronic Transitions and High Pressure Chemistry and Physics of Solids", Chapman and Hall, London, 1973.

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Their approach is to use a simple configurational coordinate model in one dimension with the assumption that this coordinate couples linear with pressure. This model explains both the linear and quadratic pressure dependence of the absorption and luminescence spectra as well as the pressure-induced broadening. Lin¹⁰ has extended this model to a multidimensional configurational coordinate model with the same basic assumptions about the coupling of the ground and excited states with pressure. Curie, Berry, and Williams¹¹ (CBW) have recently proposed that the DFS model should be modified in that the pressure coupling to the excited-state coordinate should be calculated with reference to the minimum of the excited state and not that of the ground state. This results in only a quadratic term in the pressure dependence of the absorption and emission energy in the harmonic approximation. Cubic anharmonicity would have to be introduced into the CBW model in order to give a linear pressure term to agree with the experiment. Comments by Slichter and Drickamer¹² and Curie, Berry, and Williams¹³ lead to the conclusion that the differences between these two models are not resolved. A recent paper by Berry, Tompkins, and Williams¹⁴ suggests that the lack of anharmonicity is the main problem in some of these models.

We have previously reported a study¹ of the pressure dependence of the absorption spectra of β -carotene. This model linear polyene has 11 alternate single-double bond pairs in its hydrocarbon backbone, with identical β -ionylidene rings at each end. The molecule is of interest as a prototype for the many carotenoid pigments found in nature which are important in light harvesting in photosynthesis and as a singlet oxygen quencher for photoprotection. β -carotene, being the longest naturally occurring polyene, is also a model for many properties of polyacetylene which has had recent interest as a possible organic conductor.

In our earlier study of optical absorption¹ a large red shift with pressure was observed along with broadening of the vibronic bands and an apparent increase in the intensity of the 0-0 vibronic band relative to the 0-1 vibronic band. These results were analyzed in terms of Lin's¹⁰ generalization of the DFS configurational coordinate model. We used one high-frequency mode and a set of low-frequency modes. A set of parameters that describes the coupling of pressure both to the high-frequency mode and the low-frequency modes in both ground and excited states was obtained by fitting the experimental data with this model. This fitting showed that the linear dependence of the peak position on pressure is mainly due to coupling to the high-frequency stretching modes. Because of the relative intensity change with pressure of the vibronic bands, the dimensionless normal coordinate displacement of the stretching mode between the ground and excited states was inferred to change from 1.65 at 1 bar to about 1.45 at 60 kbar. This 12% decrease is substantial.

Resonance Raman spectroscopy has recently been developed as a spectroscopic tool which can give more detailed information about excited electronic states than the more traditional tools of absorption and luminescence. Resonance Raman spectroscopy will give a much clearer picture of each active vibrational mode compared to the composite picture that is obtained in absorption and emission spectroscopy. The theoretical understanding of the resonance Raman effect has advanced to give a much clearer understanding of the various assumptions involved. One difficulty with interpretation of the resonance Raman excitation profile (RREP) is that no simple correspondence between the profile and simple parameters exists. A model calculation and fitting must in general be done to extract parameters from the data.

A multimode model^{2,15} has been developed for the analysis of the RREP and has been applied to the experimental data that

are available on β -carotene. A consistency "test" using transform techniques has been developed by Tonks and Page¹⁶ to relate the absorption spectrum to the excitation profiles if certain standard assumptions are fulfilled. Models for the resonance Raman excitation profiles are especially sensitive to linear displacements in the configurational coordinates between the minima in the ground and excited electronic states. These displacements are also called the linear coupling parameters or the Frank-Condon factors. Since these factors are expected to change with pressure in the configurational coordinate models we were led to investigate the effect of pressure on the excitation profiles of β -carotene. We previously inferred a pressure-induced decrease of about 12% in the linear coupling parameter.¹ β -carotene is a very suitable molecule for such a study since it is the classic molecule of resonance Raman spectroscopy; it has no luminescence, a very strong resonant enhancement, and relative photostability among biomolecules. Our work² on the temperature effect gives the relevant references to both the experimental and theoretical work on the resonance Raman effect on this molecule. In work that is related to the studies of β -carotene, Mathies' group has studied and modeled the excitation profile of bacteriorhodopsin¹⁷ as well as isoprene and hexatriene.¹⁸

There are three Raman modes in β -carotene that show large resonance enhancement. These are ν_1 , (C=C) stretching, ν_2 , (C-C) stretching, and ν_3 , (C-H) in-plane bending. The fitting procedure that we adopted to use with our multimode model was to fit the low-temperature absorption spectrum as well as possible. The parameters obtained from this procedure were then used to calculate a "theoretical" room temperature absorption spectrum as well as resonance Raman excitation profiles at both low and room temperature. This model has the above three high-frequency Raman-active modes and a reservoir of low-frequency inactive modes at 100 cm⁻¹. It is able to quantitatively fit the experimental data. A realistic damping constant of 50 cm⁻¹ was obtained which corresponds to a dephasing time in the picosecond time range. Since that work appeared, Chan and Page¹⁹ have done further analysis on the low- and room-temperature data and have concluded that both the excitation profile data and the absorption data satisfy the consistency "test"¹⁶ and that the broadening of the vibronic peaks in both the absorption and excitation profile spectra can be explained by thermal effects.

In the work to follow, we will present experimental data on the excitation profiles of the two strongest Raman modes (ν_1 and ν_2) of β -carotene at 70 kbar in pentane-isopentane solution. We will see that, although this data show a very large red shift in the spectral position, they show very little evidence of any significant change in the Frank-Condon factors with pressure. When the absorption and excitation profile data are analyzed by the transform techniques of Tonks and Page¹⁶ there is evidence that the standard assumptions may not be fulfilled. This research is to our knowledge the first report of a pressure study on the resonance Raman excitation profile of a molecule, although resonance Raman studies as a function of pressure have been done on semiconductors.

Experiment

The experiment was performed on a solution of *all-trans*- β -carotene (Sigma Chemical Co.) free of α isomer which was dissolved in a 1:1 mixture of reagent grade *n*-pentane and isopentane. This hydrocarbon mixture was used because it is reported²⁰ to give hydrostatic pressure up to about 70 kbar at room temperature. The concentration was made as large as possible. Considerable difficulty was encountered with pressure-induced bleaching. To avoid this problem the solvent was carefully dried

(10) S. H. Lin, *J. Chem. Phys.*, **59**, 4458 (1973).

(11) D. Curie, D. E. Berry, and F. Williams, *Phys. Rev. B*, **20**, 2323 (1979).

(12) C. P. Slichter and H. G. Drickamer, *Phys. Rev. B*, **22**, 4097 (1980).

(13) D. Curie, D. E. Berry, and F. Williams, *Phys. Rev. B*, **22**, 4109 (1980).

(14) D. E. Berry, R. C. Tompkins, and F. Williams, *J. Chem. Phys.*, **76**, 3362 (1982).

(15) Y. Fujimura and S. H. Lin, *Proc. Natl. Acad. Sci. U.S.A.*, **77**, 5032 (1980).

(16) D. L. Tonks and J. B. Page, *Chem. Phys. Lett.*, **66**, 449 (1979).

(17) A. B. Meyers, R. A. Harris, and R. A. Mathies, *J. Chem. Phys.*, **79**, 603 (1983).

(18) A. B. Meyers, R. A. Mathies, D. J. Tannor, and E. J. Heller, *J. Chem. Phys.*, **77**, 3857 (1982).

(19) C. K. Chan and J. B. Page, *J. Chem. Phys.*, **79**, 5234 (1983).

(20) G. J. Peirani, S. Block, and J. D. Barnett, *J. Appl. Phys.*, **44**, 5377 (1973).

and fresh carotene was used. The concentration was approximately $\sim 7 \times 10^{-4}$ M.

The experiment was performed in a standard design gasketed diamond anvil cell at room temperature. Two $1/5$ carat diamonds with 0.7-mm culet faces were used. The gasket was X750 Inconel with a hole of initial diameter of 0.25 mm and an initial thickness of 0.15 mm. The thickness was reduced to about 0.10 mm at 70 kbar. The pressure was determined by using the ruby fluorescence method. The Raman excitation was furnished by seven lines of an argon ion laser and by ten wavelengths from a dye laser with Coumarin 7 and Rhodamine 6G dyes.

A backscattering geometry was employed with the laser light focused into the cylindrical sample volume between the diamonds. In a separate experiment, we observed that photobleaching of β -carotene occurred in a time period of several hours with excitation of 2 to 5 mW at the peak of the absorption spectrum. We thus chose to do our Raman experiments using a power of 0.1 to 0.2 mW and to monitor the absorption spectrum at a specified wavelength both before and after each Raman scan was performed. The experiment was possible on such a small quantity of a photounstable compound only because of the very large resonance enhancement. The Raman intensities were of the order of a few hundred to a few thousand counts per second above background. These were comparable to the intensities of the diamond Raman peak which was used as the intensity standard.

Since the Raman lines of isopentane were too weak to be used as an internal standard, the Raman line of diamond at 1332 cm^{-1} was used as an appropriate "internal" intensity standard. The laser light transversed about 2 mm of diamond before coming to the sample and another 2 mm after the sample. Because of the imaging of the collection optics, it was assumed that the diamond Raman signal came only from the front diamond. This was verified in a separate experiment in which the diamond Raman signal was measured with a gasket both with and without the rear diamond. No significant change was observed.

The resonance Raman excitation profile experiment in the diamond anvil cell was first done on a β -carotene sample at nearly zero pressure. The results of that experiment when corrected for absorption agreed with other profiles done under similar conditions in more conventional geometry.² The high-pressure experiment was then performed for a range of wavelengths on two samples. The sample at 70 kbar was investigated for a more complete set of wavelengths and is reported here. The other sample at 51 kbar agreed substantially with the 70-kbar measurements. Intensity measurements at various wavelengths were repeated on these samples and had a reproducibility of $\pm 10\%$. Care was taken to ensure that the absorption of the sample did not change during the experiment.

The Raman intensities were measured relative to this diamond Raman peak and were corrected for absorption in the β -carotene sample of both the incident laser light and the Raman scattered light. Using the method introduced by Inagaki et al.,²¹ we have used the following formula for the absorption corrections on both the incident and scattered light in this backscattering geometry:

$$S(\lambda) = 2.3 \frac{\lambda_c^4 I_c [A(\lambda) + A(\lambda_c)]}{\lambda_d^4 I_d [1 - T(\lambda)/T(\lambda_c)]}$$

Here λ , λ_c , and λ_d are the wavelengths of the incident laser light and the scattered light from carotene and diamond, respectively. The Raman intensities from carotene and diamond are I_c and I_d , respectively. $A = \log I_0/I$ is the magnitude of the absorption of the carotene sample at a given wavelength. $T = I/I_0$ is the magnitude of the transmission of the sample at this same wavelength. Note that the actual thickness and concentration of the sample do not need to be known. This correction is similar to that used in resonance Raman measurements on absorbing semiconductors except that in this case we do not have an effectively infinite medium at all wavelengths as one has in the semiconductor

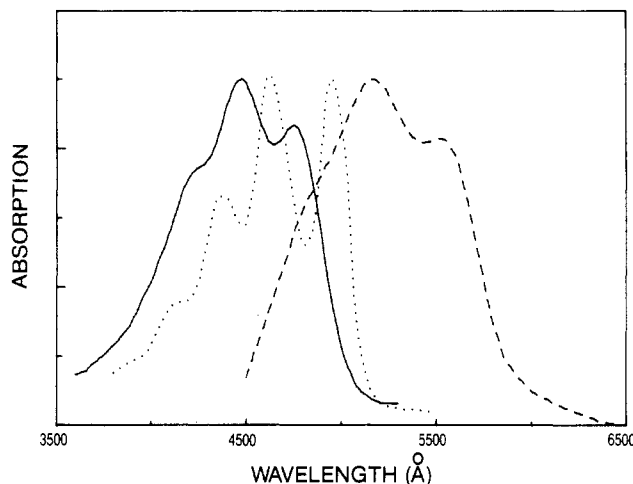


Figure 1. Absorption spectrum of β -carotene at 70 kbar and 298 K (---); 1 bar and 298 K (—); 1 bar and 118 K (···). The intensities have been normalized to the intensity of the 0-1 peak.

TABLE I: Resonance Raman Excitation Profile Data for β -Carotene at 298 K and 70 kbar^a

λ , nm	ν_1	ν_2	λ , nm	ν_1	ν_2
586.3	0.22	0.18	521.6	0.60	0.17
576.1	0.51	0.39	514.5	0.56	0.16
571.4	0.65	0.50	501.7	0.31	0.20
557.9	0.92	0.60	496.5	0.28	0.21
552.9	1.00	0.65	488.0	0.24	0.22
549.6	0.84	0.52	476.5	0.36	0.13
546.5	0.80	0.41	465.8	0.24	0.11
541.1	0.70	0.29	457.9	0.17	0.07
531.0	0.63	0.21			

^a The intensities have been normalized to the maximum intensity of ν_1 .

experiment. A separate experiment was performed on the frequency shift of the ν_1 and ν_2 Raman lines vs. pressure by using a fixed wavelength of 5145 Å .

The experiments were done with a Spectra-Physics Model 171-18 argon ion laser and a Model 375 dye laser. The spectrometer consisted of a Spex 1401 double monochromator and a cooled RCA 31034A photomultiplier with SSR photon-counting electronics. The data acquisition was done on a Canberra Series 30 multichannel analyzer which allowed the direct determination of peak areas.

Results

The absorption spectra at the three different conditions relevant to this research are shown in Figure 1. These conditions are (1) 1 bar and -155 °C , (2) 1 bar and 25 °C , and (3) 70 kbar and 25 °C . The 0-0 and 0-1 peaks are at 496.5 and 463.6 nm for case 1, 474.2 and 446.8 nm for case 2, and 554.4 and 516.6 nm for case 3. The main observable effect of pressure on the absorption spectra is that the peaks are red-shifted by about 3000 cm^{-1} and the vibronic bands are broadened. Pressure produces an apparent increase in the intensity of the 0-0 band relative to the 0-1 band. This change is consistent with our previous study¹ of the effect of pressure on the absorption spectrum of β -carotene up to 54 kbar. In Figure 1 we can also see that the low-temperature data² is red-shifted by about 1000 cm^{-1} from the data at room temperature and room pressure and that the vibronic bands are much narrower.

The resonance Raman excitation profiles for the fundamental bands ν_1 and ν_2 are given in Table I. There is a large red shift similar to that seen in the absorption spectrum with the large peak occurring at nearly the same position as the 0-0 absorption peak. Figures 2 and 3 show the comparison of the experimental data on the excitation profile for ν_1 and ν_2 at the three different conditions. The excitation profile data at low and room temperature at 1 bar is taken from our earlier work.² These three spectra have

(21) F. Inagaki, M. Tasumi, and T. Miyazawa, *J. Mol. Spectrosc.*, **50**, 286 (1974).

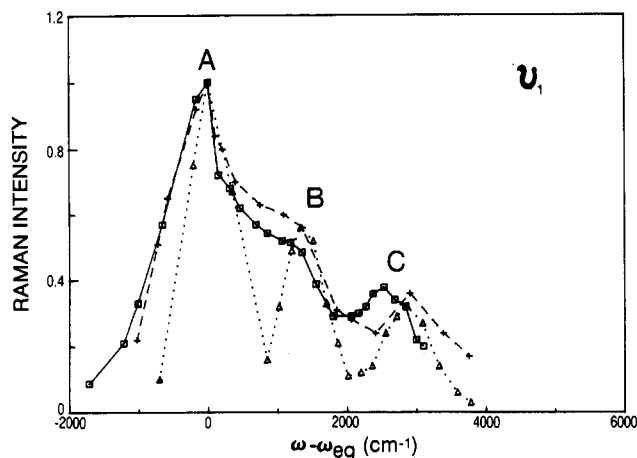


Figure 2. Experimental resonance Raman excitation profiles of the ν_1 mode of β -carotene: 70 kbar and 298 °C (+); 1 bar and 298 K (□); 1 bar and 118 K (Δ). These spectra are plotted as a function of displaced frequency ($\omega - \omega_{eg}$) where ω_{eg} is the frequency (cm^{-1}) of the 0-0 vibronic peak as observed in absorption. The intensities have been normalized to the maximum of peak A. Peaks A, B, and C are discussed in the text.

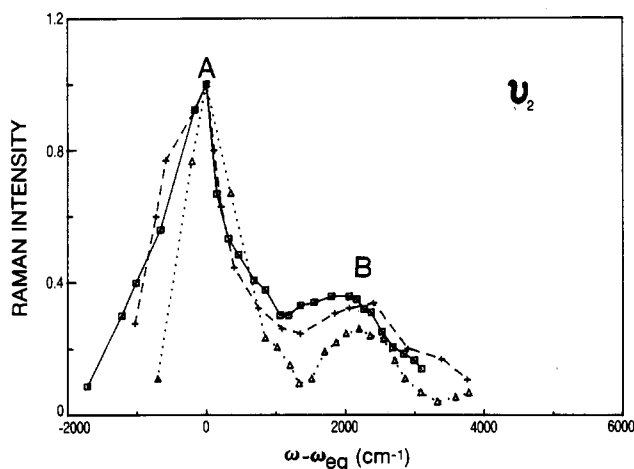


Figure 3. Experimental resonance Raman excitation profiles of the ν_2 mode of β -carotene: 70 kbar and 298 K (+); 1 bar and 298 K (□); 1 bar and 118 K (Δ). These spectra are plotted as a function of displaced frequency ($\omega - \omega_{eg}$) where ω_{eg} is the frequency (cm^{-1}) of the 0-0 vibronic peak as observed in absorption. The intensities have been normalized to the maximum of peak A. Peaks A and B are discussed in the text.

been plotted on a wavenumber scale which has in each case been shifted to match the 0-0 vibronic peaks of the corresponding absorption spectra. The intensity of the excitation profiles has been normalized to the maximum peak intensity of the ν_1 profile in each case. The data at low temperature show three peaks in ν_1 which are labeled A, B, and C. The ν_2 profile at low temperatures shows two peaks which are labeled A and B. The dip between the A and B peaks in the low-temperature ν_1 profile becomes a shoulder in the room pressure, room temperature 1-bar data as well as in the high-pressure data. The profiles at 70 kbar have a shape similar to those at 1 bar, but they show broader features and less structure in comparison with the excitation profiles at room temperature. There is little relative intensity change between the ν_1 and the ν_2 excitation profiles produced by pressure. It should be noted that in all cases the excitation profiles show narrower structure than the corresponding absorption spectrum. We will analyze these excitation profiles in the following section. The resonance Raman scattering intensity from the ν_3 mode was too weak in the diamond anvil cell to obtain usable intensity data. We do, however, report the position of the ν_3 mode as a function of pressure.

The frequencies of the fundamental bands at 70 kbar are ν_1 , 1551 cm^{-1} , ν_2 , 1179 cm^{-1} , and ν_3 , 1022 cm^{-1} . Results on the frequency of these modes as a function of pressure are shown in

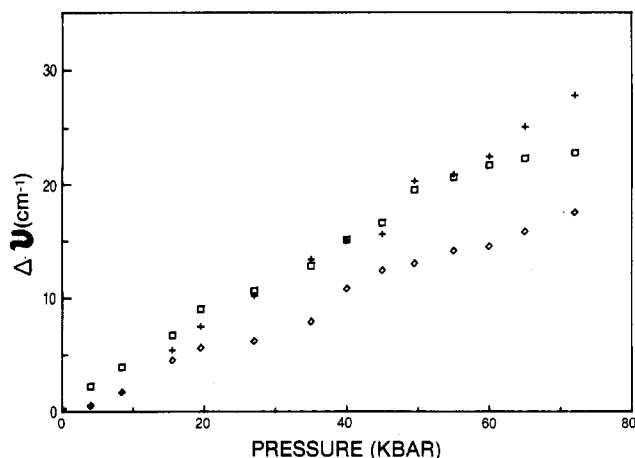


Figure 4. Pressure dependence of Raman mode frequencies of β -carotene. Changes relative to the zero pressure values are shown for ν_1 (+), ν_2 (□), and ν_3 (◇). See text.

TABLE II: Parameters Obtained by Fitting the Multimode Model to the Absorption Spectrum Which Were Then Used in Calculation of the Excitation Profiles

	$P = 1 \text{ bar}^a$	$P = 70 \text{ kbar}$
Δ_1	1.20	1.12
Δ_2	0.90	0.80
Δ_3	0.70	0.62
$\bar{\omega}$, cm^{-1}	100	100
S	9	10
γ , cm^{-1}	50	50

^a Reference 2.

Figure 4. These data have been fit to second-order polynomials in pressure. The results of these fittings are

$$\nu_1 = (0.36 \pm 0.02)P + (0.5 \pm 0.3)P^2$$

$$\nu_2 = (0.46 \pm 0.02)P - (0.19 \pm 0.03)P^2$$

$$\nu_3 = (0.27 \pm 0.02)P - (0.4 \pm 0.2)P^2$$

where $\Delta\nu$ is in cm^{-1} and P is in kbar.

Analysis and Discussion

The experiment that we have done was mainly motivated to see if some more information could be gained about the exact mechanism of the pressure effect on the electronic states of a molecule. In our earlier pressure study¹ we had concluded that there was a pressure-induced decrease of 12% in the displacement between the minima in the excited- and ground-state configurational coordinates for the one high-frequency normal mode used in this model.

In order to provide a check on this hypothesis we will analyze the present absorption and excitation profile data using the same modeling procedure that we used in our earlier study² on the effect of temperature. The model used there was a multimode model with three high-frequency modes and a reservoir of low-frequency modes. In that work we obtained the best set of parameters by fitting the low-temperature absorption spectrum. The parameters obtained by this procedure are given in Table II. Using these parameters we were able to satisfactorily reproduce both the low-temperature and room-temperature excitation profiles. The broadening at room temperature is accounted for by the increasing number of phonons in the low-frequency (100- cm^{-1}) modes.

Since the spectra at room temperature at both room pressure and at high pressure have similar vibronic structure, we will vary only the dimensionless normal coordinate displacements and the parameter relating to the strength of the coupling to the low-frequency modes. Our procedure is to fit our high-pressure absorption spectrum and then obtain calculated excitation profiles. One should refer to our earlier paper² for the details of our model and procedure. Following that method, a fit to the high-pressure

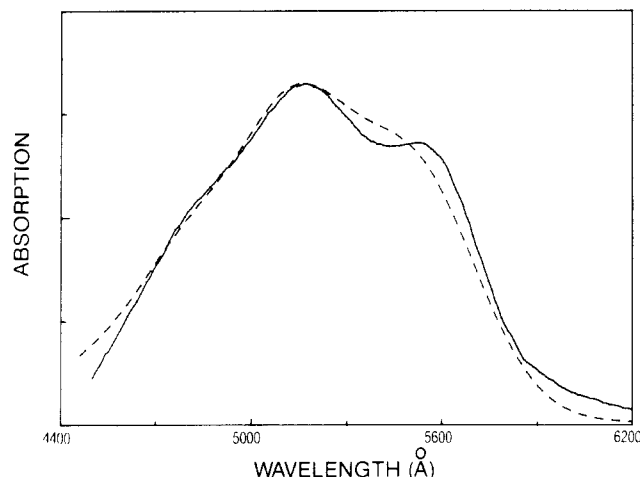


Figure 5. Absorption spectra at 70 kbar and 298 K. Calculated from multimode theory (---); experiment (—).

absorption spectrum was made which is shown in Figure 5. We also varied the damping constant, γ , and obtained the best fit with the same value as used previously. The model parameters that were obtained in this fitting are given in Table II. The results of these fits show that all the dimensionless linear coupling parameters decrease by about 0.1 while the strength, S , of the coupling to the low-frequency modes increases by 10%. In such a fitting procedure there always are questions as to how sensitive the fit is to the various parameters. In the present case the uncertainty in the normal coordinate displacements is of the order of 0.05. Thus the inferred decrease in the normal coordinate displacements are just the sum of their joint uncertainties. The other parameter that is quite sensitive to the fit is the damping constant. The use of γ smaller than 30 cm^{-1} makes the 0-0 peak stronger than the 0-1 peak in the absorption spectrum. A γ larger than 80 cm^{-1} makes the absorption spectrum to have too strong of a 0-1 peak.

These parameters were then used to calculate predicted excitation profiles which are shown in Figure 4. One can see that the fit is satisfactory although not as good as one would wish if a more general fitting procedure were adopted. We conclude from this fitting procedure that much smaller or even zero decreases in the linear coupling parameters are obtained than our earlier work indicated. This suggests that our previous fitting procedure using only one high-frequency mode in a phenomenological model and relying on small intensity changes in the vibronic peaks gives an unreliable measure of what is happening with pressure.

Our present analysis seems to indicate that there is a very small or perhaps zero decrease in the linear coupling parameters with pressure. However, this conclusion does not lead to a definitive statement about the applicability of the DFS or the CBW configurational coordinate models to pressure effects on the molecular electronic spectra of β -carotene.

Another method of analysis will be to compare the absorption spectrum and excitation profiles by using the transform technique of Tonks and Page.¹⁶ This technique will tell if the standard assumptions that are commonly used in resonance Raman models are fulfilled for our data independent of the details of the model. These standard assumptions are (1) the adiabatic and Condon approximations, (2) a single electronic excited state, (3) harmonic vibrations (phonons), (4) linear electron-phonon coupling, and (5) identical molecules (no inhomogeneous broadening). The multimode model used above and in our analysis of the temperature effects² fulfills these assumptions. Chan and Page¹⁹ have recently used this test on our low-temperature and room-temperature data on β -carotene and have shown that the transform technique works very well on both sets of low-pressure data. We have applied this technique using the high-pressure absorption spectrum and the high-pressure Raman frequencies as input and have calculated the expected excitation profiles. The results of this are shown in Figure 7. The transformed excitation profiles

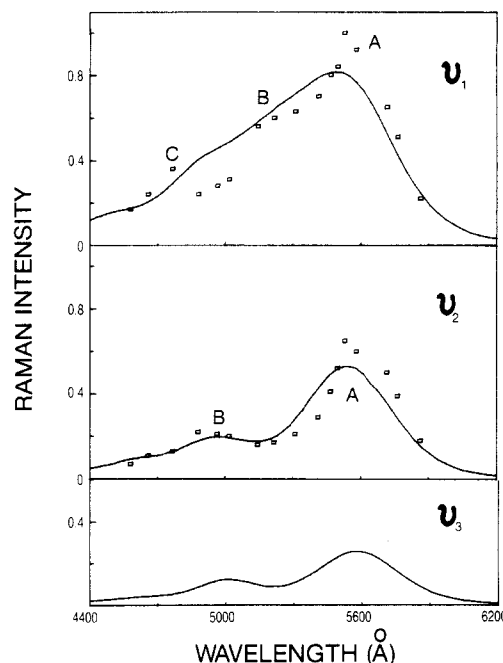


Figure 6. Resonance Raman excitation profiles of β -carotene: ν_1 (top), ν_2 (middle), and ν_3 (bottom). Experimental values (\square), multimode calculation (—). The intensities have been normalized to peak A in the ν_1 profile.

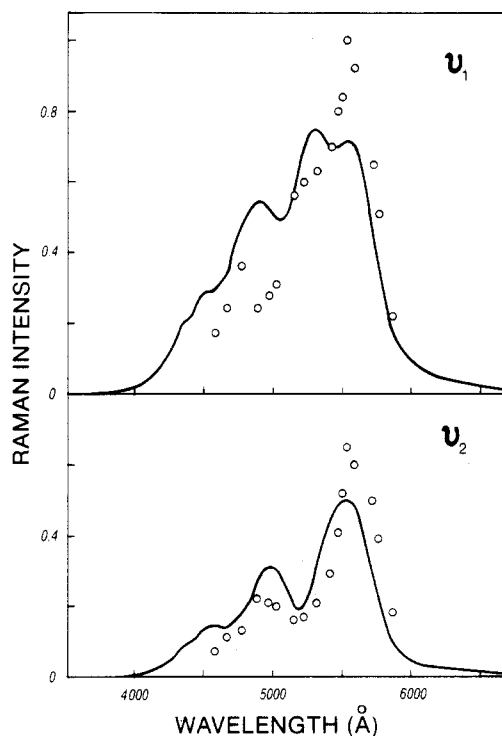


Figure 7. Resonance Raman excitation profiles of β -carotene: ν_1 (top) and ν_2 (bottom). Experimental values (\square), profiles transformed from experimental absorption spectrum by the technique of Tonks and Page (ref 16) (—).

do not seem to fit as well as the same method did when applied to the room pressure data. The transform predicts a strong B peak in the ν_1 profile while in the experiment the B shoulder that exists at room pressure remains a shoulder in the high-pressure data. This B region is due to interference effects and is particularly sensitive to small deviations from the standard assumptions.

This failure of the transformed profiles to agree with the experimental profiles suggests to us that some of the standard assumptions may no longer be completely fulfilled in the high-pressure experiment. In particular, inhomogeneous broadening

may play an important role which of course would enter into models for the absorption spectrum and for the excitation profiles in different ways. We conclude that the high-pressure excitation profile data may show some evidence of inhomogeneous broadening that was not present in our earlier studies at 1 bar.

The question remains then as to what causes the large red shift in the electronic spectrum of β -carotene as pressure is applied. Although the use of configurational coordinate models cannot be ruled out by the present work, our opinion in this case is that probably the solvent theories would be the most appropriate. The solvent models have not been worked out in enough detail to explain pressure-induced solvent changes on resonance Raman excitation profiles.

Since both the Tonks and Page transform test and our own multimode modeling give only a fair fit to the experimental excitation profiles at high pressure, we are led to suggest that more theoretical modeling is needed with the inclusion of inhomogeneous broadening in the model. This might be able to explain the fact that our experimental excitation profiles are not in very good agreement with the present modeling.

Summary

In this work, experiments have been performed on the resonance Raman excitation profiles of the two strongest vibrational modes,

ν_1 and ν_2 , of β -carotene in a diamond anvil cell at a pressure of 70 kbar. The β -carotene was dissolved in a 1:1 pentane-isopentane mixture. The large red shift in the absorption spectra is reflected in the excitation profiles. The shape and details of the excitation profiles at high pressure are similar to the profiles at low pressure and room temperature except for a slight amount of broadening. We have applied a multimode model to the absorption data and have concluded that only rather small decreases in the linear coupling parameters are necessary to fit the data. These parameters when used to calculate the excitation profiles give a fair agreement with the experiment. We have also used the transform technique of Tonks and Page to compare the absorption spectrum with the excitation profile in a model free way. This transform method fails suggesting that inhomogeneous broadening may be present in the high-pressure experiment.

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A Thorough Study of Bromide Control in Bromate Oscillators. 2. Simulation by the Oregonator Model of the Behavior of Reacting Belousov-Zhabotinsky Systems Perturbed by Bromo-Complex-Forming Metal Ions

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The behavior of BZ oscillators in the presence of thallium(III)—a bromide-removing ion—can be simulated by the Oregonator model if the dynamic bromide concentration conditions prevailing in the reacting systems, the rate of formation and dissociation of thallium(III) bromo complexes, are considered. The respective rate constants were obtained from correlations known for ligand substitution reactions. Preliminary studies on mercury(II)-containing BZ systems also indicate that the effects induced by this ion on the BZ oscillators can likely be simulated by the same model.

Introduction

In our previous paper¹ we have reported how thallium(III) ions influence the behavior of bromate oscillators. Our investigations revealed that at low thallium(III) concentrations (1×10^{-5} – 6×10^{-5} M) the time of oscillation increased with an increase in thallium(III) concentration and about 8×10^{-5} M thallium(III) completely quenched the oscillation. At high thallium(III) concentrations ($\sim 10^{-2}$ M), however, the reacting systems again showed oscillatory behavior: high-frequency oscillations were recorded which lasted only for a short period of time. The effect induced by thallium(III) ions was explained in terms of their bromo-complex-forming ability considering the stability constants of thallium(III) bromo complexes. The time increasing effect of low concentrations of thallium(III) has been attributed to the buffering of the bromide ion concentration by the bromo complexes of thallium(III), and a qualitative explanation has been put forward. However, the phenomenon appearing at high thallium(III) concentrations could not be accounted for.

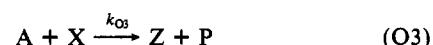
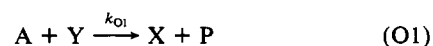
In our previous paper we regarded the formation of the bromo complexes of thallium(III) as a much faster process than the formation of bromide ions in the autocatalytic step of the Belousov-Zhabotinsky (BZ) reaction and, therefore, considered only equilibrium bromide concentrations. These were calculated from

known formation constant values. The calculated equilibrium bromide concentrations were always below the critical bromide concentration and therefore we could not explain the occurrence of oscillations at high thallium(III) concentrations.

Based mainly on the experimental results described in our previous paper¹ we thought that chemical oscillations observed in the presence of bromide-removing ions (Tl^{3+} , Hg^{2+} , and Ag^{+}) can be accounted for in terms of bromide control, and thus the Oregonator model can be used if the dynamic bromide concentration conditions prevailing in the reacting systems, the rate of formation and dissociation of the metal bromo complexes, are considered.

Calculations

The irreversible Oregonator² consists of the following five steps:



(1) Körös, E.; Varga, M. *J. Phys. Chem.* 1984, 88, 4116–21.