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# Resonance Raman Spectroscopy

There are few techniques available to chemists today that have the wide range of applicability inherent to Resonance Raman Spectroscopy (RRS). By employing RRS it is possible to study reactions taking place at the surface of electrodes (*1–4*), obtain structural information from deep within complex biological molecules (*5–6*), determine the shapes of potential surfaces (*7*) and molecular geometries (*8*) in excited states, record spectra of species with half-lives on the $\mu$ sec level (*9*), obtain highly accurate values for physical parameters such as anharmonicity coefficients (*10*), and monitor reactions on catalytic surfaces (*11*). The preceding list is not meant to be complete, but only to give the reader an idea of the wide utility of RRS.

In the past the situation for Raman spectroscopists was not this advantageous. Early work, in what is referred to as normal Raman Spectroscopy (NRS), used a low pressure mercury arc as the source of electromagnetic radiation. Experiments involving NRS usually required neat liquids or solutions with concentrations greater than 0.1 $M$ and rather large volumes of sample in order to obtain reasonable signal to noise ratios. These limitations were largely overcome with the advent of laser sources whose powerful output could be focused into a very small volume of sample. Using the laser, samples in the $\mu$l and mM ranges can be readily studied.

Early Raman measurements were made on compounds which were selected such that the Hg exciting lines fell far short of the first excited electronic states. This was necessary since absorption would result in local heating effects and consequently sample decomposition. Now this difficulty is circumvented by using the rotating sample technique combined with laser sources as first suggested by Kiefer and Bernstein (*12–13*). Since the laser beam can be focused on only a small portion of the rotating sample, local heating is minimized. When the exciting line is "tuned" into an electronic absorption band, some of the Raman bands which are related to the electronic transition that is responsible for the absorption will be greatly enhanced. Since the intensity of these lines can be tremendously increased under resonance conditions, samples as dilute as $10^{-7}$ $M$ can be studied (*14*). The fact that only certain Raman bands are enhanced when the exciting line is in resonance with an electronic band imparts a selectivity to the effect. This selectivity has some rather important ramifications as will be discussed later in this article. The recent development of CW tunable dye lasers gives an added dimension to the field. Now the electronic absorption band may be "scanned" with different exciting frequencies much as has been done in fluorescence spectroscopy for years.

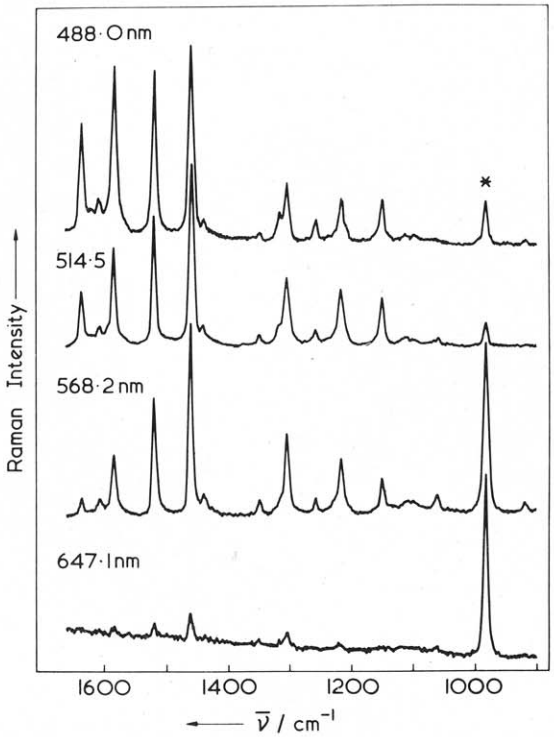


Figure 1. Raman spectra of the $[Fe(o\text{-phen})_3]^{2+}$ ion in the 1600–900 cm$^{-1}$ region. Spectral slit width, 2–3 cm$^{-1}$. * indicates the 983 cm$^{-1}$ reference band of the sulfate ion.

An example of RR enhancement is given in Figure 1 where the Raman spectrum of $1.0 \times 10^{-4}$ $M$ tris($o$-phenanthroline)-iron(II) sulfate in water is shown as obtained with four different exciting lines (*15*). An internal standard of 0.5 $M$ $SO_4^{2-}$ gives rise to the band at 983 cm$^{-1}$. Clearly, as the source approaches higher frequencies the Raman bands are strongly enhanced. Deciding at which frequency the bands maximize is less straightforward since intensity corrections must be made for: self-absorption, that is to say the reabsorption of Raman scattered radiation that still falls within the absorption band of the sample (*16*); detector sensitivity, since the detector response is not constant over the range of frequencies studied, and the $\nu^4$ scattering dependence of the normal Raman effect.

This article will now present some very rudimentary theory as a background for RRS and the understanding of a few rather interesting examples of the applications that have been reported in the literature.

## Theory

In NRS, the scattered intensity due to a vibrational transition closely follows a $\nu^4$ dependence

$$I \approx (\nu_0 \pm \nu_k)^4 \tag{1}$$

where $\nu_0$ is the frequency of the exciting radiation, $\nu_k$ is the frequency of the $k$th vibrational mode, and the plus/minus refers to the anti-Stokes and Stokes radiation, respectively (see Fig. 2*a*). Theory (*17–18*) has predicted that the total Raman intensity scattered over the solid angle $4\pi$ by randomly oriented molecules is given by the expression

$$I_{gk,gj} = \frac{2^7\pi^5}{3^2c^4} I_0 \sum_{\rho,\sigma} |(\alpha_{\rho\sigma})_{gk,gj}|^2 (\nu_0 \pm \nu_k)^4 \tag{2}$$

where $I_0$ is the incident intensity and

$$(\alpha_{\rho\sigma})_{gk,gj} = \sum_{r,v} \frac{(M_\rho)_{gk,rv}(M_\sigma)_{rv,gj}}{\nu_{rv,gk} - \nu_0 + i\Gamma_{rv}} + \frac{[\sigma \leftrightarrow \rho]^1}{\nu_{rv,gj} + \nu_0 + i\Gamma_{rv}} \tag{3}$$

[1]The numerator is the same as the first term except that $\sigma$ and $\rho$ are reversed.

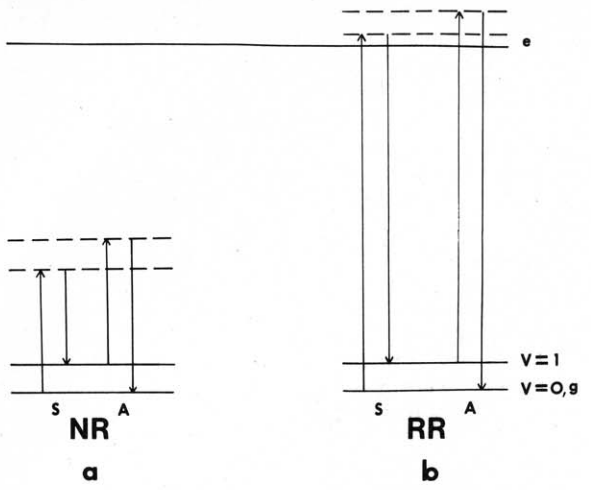


Figure 2. Energy level diagrams for Raman effects; S = Stokes, A = antiStokes. (a) Ordinary Raman effect. (b) Normal resonance Raman effect.

$(\alpha_{\rho\sigma})_{gk,gj}$ is referred to as the $\rho\sigma$th component of the Raman scattering tensor (where $\rho,\sigma = x,y,$ or $z$); $g$ and $r$ refer to the ground and any excited electronic state, respectively, $k,v$ and $j$ are vibrational quantum numbers, $\Gamma_{rv}$ is a damping constant which has been loosely correlated with the half-width of a given excited state and $(M_\rho)_{a,b}$ refers to the $\rho$th component of the electronic transition moment from state $a$ to $b$. The summation formally runs over all excited states and cannot be evaluated analytically unless some rather critical assumptions are made. For the case of RRS (see Fig. 2*b*) certain terms in the summation may become extraordinarily large (e.g. . . . where $\nu_0$ approaches $\nu_{rv,gk}$, (see eqn. (3)), the net result being that the observed intensity follows a complex $\nu$ dependence. In NRS where the exciting frequency is far removed from the first excited state (see Fig. 2*a*), the result of the summation may be considered a constant since small changes in $\nu_0$ will not greatly favor any particular term. In that case the origin of the $\nu^4$ dependence is clearly understood (see eqn. (2)).

In order to understand the origins of the RR effect we will consider a molecule with just two low-lying excited electronic states, $e$ and $s$, and the changes in intensity that occur when the exciting frequency is moved into resonance with the lower state $e$. Under these conditions, the basic approach of Albrecht (*19*) may then be employed in a manner similar to the treatment by Inagaki et al. (*20*), where consideration of the dependence of the electronic transition moments on the normal vibrational modes leads to an expression for the elements of the scattering tensor of the following form

$$(\alpha_{\rho\sigma})_{gk,gj} = A + B \tag{4}$$

where

$$A = [\langle g|\rho|e\rangle\langle e|\sigma|g\rangle/h]f_A \tag{5}$$

$$B = [\langle g|\rho|e\rangle \cdot h_{es}{}^a \cdot \langle s|\sigma|g\rangle/h^2(\nu_s - \nu_e)]f_B \tag{6}$$

$$f_A = \sum_v \frac{\langle k|v\rangle\langle v|j\rangle}{\nu_{ev,gk} - \nu_0 + i\Gamma_{ev}} \tag{7}$$

$$f_B = \sum_v \frac{\langle k|v\rangle\langle v|Q_a|j\rangle + \langle k|Q_a|v\rangle\langle v|j\rangle}{\nu_{ev,gk} - \nu_0 + i\Gamma_{ev}} \tag{8}$$

$$h_{es}{}^a = \left\langle e\left|\frac{\partial H}{\partial Q_a}\right|s\right\rangle \tag{9}$$

and $\nu_s - \nu_e$ is the frequency corresponding to the difference between states $e$ and $s$. All of the integrals listed above are of the general type $\langle a|F|b\rangle$, where $F$ can take any of the following forms

1) $F = 1$; simple overlap integral
2) $F = \rho$ or $\sigma$; integral corresponding to a pure electronic transition moment
3) $F = Q_a$; integral corresponding to a vibrational transition moment. ($Q_a$ is a normal coordinate)
4) $F = (\partial H/\partial Q_a)$; integral corresponding to the degree of coupling of states $a$ and $b$ through the normal mode $Q_a$

As the source is "tuned" into the $e$ absorption band, the $A$ term will describe the behavior of the intensities of totally symmetric modes since the product of the integrals $\langle k|v\rangle$ and $\langle v|j\rangle$ in eqn. (7) can be finite due to the non-orthogonality of vibrational wavefunctions in the ground and excited states of totally symmetric vibrations. Then the intensity of totally symmetric vibrations can increase as the exciting frequency comes into resonance with the lowest excited state. For non-totally symmetric modes the vibrational wavefunctions are more nearly orthogonal and thus these modes may only derive their intensity from interactions described by the $B$ term. Consideration of the form of $B$ clearly indicates that the single most important factor for resonance enhancement is the value of $h_{es}{}^a$. Thus if two excited states are efficiently coupled by a given normal mode, that normal mode can be expected to be enhanced to a large extent. Application of group theoretical principles quickly answers the question of whether or not $h_{es}{}^a$ will be finite, since in order for the integral to be non-zero, $\Gamma_e \otimes \Gamma_a \otimes \Gamma_s$ must contain the totally symmetric representation. Here we can clearly see part of the reason for the inherent selectivity of RRS. This selectivity also shows itself with respect to totally symmetric modes as it is quickly observed that only those vibrational modes involving bonds affected by the change in electronic state are enhanced. For example in the case of Fe(II)-$\alpha$-diimine complexes, an electronic band in the visible region is known to be due to charge-transfer from the metal to the ligand. This charge is localized in the skeletal region. When the Raman spectrum is obtained with radiation that falls within this visible band, only $\alpha$-diimine skeletal modes are enhanced (*15*) (see Fig. 1).

One final point to be made is that $B$-type enhancement is usually smaller than $A$-type due to

1) the additional factor $(\nu_s - \nu_e)$ in the denominator of the $B$ term (see eqn. (6))
2) the additional factor $(h_{es}{}^a)$ in the numerator of the $B$ term (see eqns. (6) and (9))

Taken together, these terms merely reflect the fact that B-type enhancement requires efficient coupling of nearby electronic states, which is less common than A-type enhancement via resonance with a single electronic state. These considerations account for the observation that for most molecules studied to date, only symmetric modes have been resonance enhanced.

## Applications

### *Vibrational Frequencies in Excited States*

It has been demonstrated by Ohta and Ito (*7*) in a study of quinoxaline, that measurements of the intensities of Raman lines taken at different excitation wavelengths can be used to assign excited state frequencies of non-totally symmetric modes. An earlier work (*21*) on quinoxaline which employed the usual approach of vibrational analysis of electronic spectra, assigned excited state frequencies to three of the $b_1$ modes as shown in the second column of the table. These assignments were made by employing the concept of "parallel correspondence" from the ground to excited states. The expression "parallel correspondence" merely implies that in going from the ground to the excited state, the order of vibrational frequencies will not be changed. Ohta and Ito were able to show qualitatively that the strongest band observed in the vibronic spectrum should undergo the greatest frequency change between the excited and ground states. Since the $n \rightarrow \pi^*$ absorption spectrum of quinoxaline is dominated by a 425 $cm^{-1}$ band they concluded that the reported 62 $cm^{-1}$ shift of frequency (425 → 487 $cm^{-1}$) was too small. Starting from the vibronic theory of the Raman effect as set forth by Albrecht

$B_1$ Vibrational Assignments for Quinoxaline ($cm^{-1}$)

| Ground State | First Excited State[a] | First Excited State[b] |
|---|---|---|
| 867 | 600 | 425 |
| 796 | ...[c] | 600 |
| 718 | ...[c] | ...[c] |
| 487 | 425 | ...[c] |
| 398 | 310 | 310 |

[a] Jordan et al. (see Ref. (*21*)).
[b] Ohta and Ito (see Ref. (*7*)).
[c] Values not reported.

(*19*), Ohta and Ito showed that the intensity enhancements of the non-totally symmetric vibrations were related to the differences of their frequencies in the excited and ground states through the $h_{es}{}^a$ term (see also eqn. (6))

$$\nu^2 - \nu'^2 = \frac{1}{4\pi^2 c^2} \frac{2|h_{es}{}^{b_1}|^2}{E_e - E_s} \tag{10}$$

The primed term refers to the excited state frequency. Measurements of the relative intensities showed that the ratios of the coupling terms (in this case: $\langle {}^1B_1|\partial H/\partial Q|{}^1A_1\rangle$) for the 867,796,487 and 398 $cm^{-1}$ lines should be 4.2:1.7:0:1. On this basis they proposed the assignments given in column 3 of the table. In support of their conclusion they pointed out that the 867 $cm^{-1}$ mode is due to an out-of-plane C—H bending motion which is similar to that motion found in pyrazine, whose frequency decreases from 925 to 385 $cm^{-1}$ as a result of vibronic coupling (*22*).

### *Determination of Molecular Geometry in an Excited State*

Hirakawa and Tsuboi (*8*) have postulated the empirical rule that if a Raman line becomes stronger when the exciting frequency is brought into resonance with an electronic band, this means that the equilibrium conformation of the molecule is distorted along the normal coordinate of the given Raman line in the transition from the ground to excited electronic state. The most striking example that is presented in their article is the case of gaseous $NH_3$ where on changing from an exciting line of 514.5 nm to one of 351.1 nm the intensity of the umbrella vibration ($\nu_2$, 930 $cm^{-1}$) is enhanced ten times more than that of the symmetric stretch. This is exactly what is expected since the first excited electronic state of $NH_3$, which lies at 216.8 nm above the ground state, is known to be planar (*23*). Although this is an extremely simple case, the possible uses of intensity information such as this are obvious.

### *Overtones in Resonance Raman Spectra*

One of the unique features of a normal Raman spectrum is the general absence of overtones and combination bands. When, however the exciting line coincides with an electronic absorption band, simple molecules, such as $I_2$ and $TiI_4$, frequently exhibit long, well-defined progressions of overtones corresponding to totally symmetric modes. Indeed, the intensity of the first overtone may be nearly equal to that of the fundamental. Kiefer and Bernstein (*24*) observed 15 overtones for $I_2$ in the gas phase. An interesting sidelight to this was that Bernstein (*25*) was able to observe RR scattering of gaseous $I_2$ when using radiation of 488.0 nm and resonance fluorescence when using 514.5 nm radiation. The latter is on the order of $10^3$ times stronger than RR scattering and would overshadow it in all cases if not for the quenching which occurs in solutions.

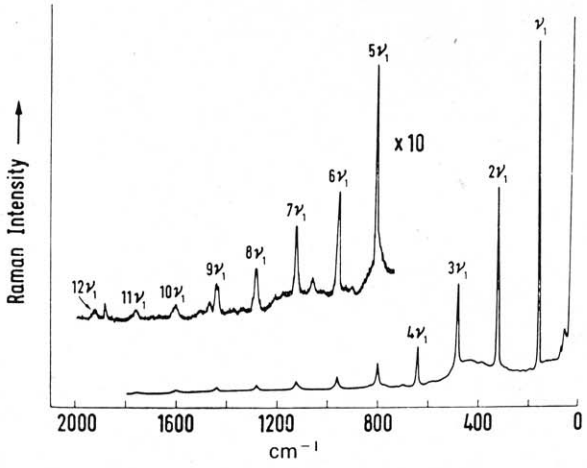


Figure 3. Resonance Raman spectrum of solid $TiI_4$ (514.5 nm excitation) (Clark and Mitchell, Ref. (*10*))—reproduced by permission of the authors.

Clark and Mitchell (*10*) observed as many as 9 overtones in the RR spectrum of $TiI_4$ in solution and 11 overtones in the solid state (see Fig. 3). There is a useful academic application possible using these long overtone progressions, that being the calculation of harmonic frequencies and anharmonicity constants. The latter describes the deviation of a vibration from the simple harmonic approximation while the former is the frequency the mode would exhibit if truly harmonic. These parameters may be obtained to a high degree of accuracy from the relationship (*26*)

$$\nu(n) = n\omega_1 - X_{11}(n_2 + n) + \ldots \tag{11}$$

where $\nu(n)$ is the observed wavenumber of any overtone, $\omega_1$ is the harmonic frequency, $X_{11}$ is the anharmonicity constant and $n$ is the vibrational quantum number. A plot of $\nu(n)/n$ versus $n$ will then give a straight line with a slope equal to $X_{11}(n + 1)$ and an intercept equal to $\omega_1$. An exercise of this type, employing published spectra, would seem to be appropriate for use in an elementary instrumental analysis or physical chemistry course.

### *Studies of Unstable Species*

Two different approaches have been taken to study unstable species by RRS. One, reported by Woodruff (*27*), employs a standard continuous flow apparatus which sends the reaction mixture through a capillary tube that lies at the focal point of the laser. Using this method in a study of the system consisting of horseradish peroxidase and hydrogen peroxide it was shown that intermediates having half-lives on the order of 0.06 s could readily be studied by RRS.

The second approach was that of Pagsberg et al. (*9*) who studied the radical anion of terphenyl($TP^{\cdot -}$). This radical anion has a stability that is strongly dependent on the nature of the solvent and counterions. Stable solutions can be obtained by reducing *p*-terphenyl with sodium in tetrahydrofuran while a short-lived $TP^{\cdot -}$ can be produced by pulsed radiolysis of a solution of *p*-terphenyl dissolved in a mixture of ethanol and ethylenediammine. The RR technique in this application involved the use of a flash lamp pumped dye laser as a source, with an optical multichannel analyzer for signal detection. Dye laser pulses from Coumarin 102 (481.61 nm) of 10 mJ and 600 ns duration were focused onto a spot of 0.25 mm diameter within the cell. This exciting frequency falls on the red side of an electronic absorption band with a maximum at 470.0 nm. One of the enhanced Raman lines (1593 $cm^{-1}$) of $TP^{\cdot -}$ was found to be comparable in intensity to the 1454 $cm^{-1}$ ethanol line while the $TP^{\cdot -}$ concentration was only $4 \times 10^{-5}$ *M*. This particular line was found to be observable even at a $TP^{\cdot -}$ concentration of $8 \times 10^{-6}$ *M*. The result is particularly impressive considering the fact that the half-life of $TP^{\cdot -}$ under their experimental conditions was ~2$\mu$ s. Frequencies of the $TP^{\cdot -}$ bands thus obtained were then compared to those of $TP^{\cdot -}$ under stable conditions and found to be in excellent agreement.

### *Biological Systems*

Perhaps the greatest interest in RRS has involved the study of biologically significant molecules. Since there are a number of excellent reviews available (*5, 6*) we will only touch on a few of the many applications of RR in this area. The RR process lends itself to this area since the nature of the effect is such

that only modes associated with the chromophoric group of a molecule are enhanced (*17*). The consequences of this are immediately obvious

1) Vibrational modes of chromophoric groups in biological molecules, which are often the sites of their biological activities, will be strongly enhanced.
2) The remainder of the vibrational modes will not be enhanced and therefore cannot complicate the spectra.
3) Due to the increased sensitivity of the effect, spectra can be obtained under physiologically relevant conditions.

In sum then, we have a useful biological probe that is both highly selective and extremely sensitive.

Heme related systems have received the most attention from spectroscopists. For example, the spin and oxidation states of Fe atoms in hemoglobin and cytochrome-*c* can be determined rather simply from the frequency shifts of RR enhanced modes (*28*). The appearance of a band showing inverse polarization (for a discussion of inverse polarization see ref. (*6*)) at ~1580 $cm^{-1}$ is indicative of low-spin Fe in both the Fe(II) and Fe(III) states (*28*). This band shifts to ~1553 $cm^{-1}$ in high-spin complexes. In cytochrome-*c* and other heme proteins, a band at ~1360 $cm^{-1}$ indicates Fe(II); while if the Fe is oxidized to Fe(III) the band shifts to 1375 $cm^{-1}$. More extensive tables of frequency correlations for hemes are available in the literature (*5, 6, 29*).

The interaction of dyes with biological substrates can also be investigated via RRS. Cary et al. (*30*), in an investigation of the interaction of methyl orange (MO) dye with bovine serum albumin (BSA), studied the spectrum of aqueous, solid and BSA complexed to MO. On the basis of the great similarity of the solid and complex spectra they were able to conclude that the MO was buried within the protein rather than adsorbed on its surface.

### *Spectroelectrochemistry*

The detection and study of electrogenerated species through the use of spectroscopic methods is well documented (*31*). Foremost among the methods employed are those of electron spin resonance (ESR) and uv-visible spectroscopies. ESR is severely limited by the requirement that the species under study must be paramagnetic and uv-visible spectroscopy, while not limited to paramagnetic compounds, usually contains little structural information. Infrared spectroscopy should theoretically reveal much structural information but its application is limited due to the small spectral window available when water is used as a solvent.

Now, an entirely new field has been opened up by Jeanmaire and coworkers (*1–3*) who have applied RRS to the study of electrogenerated species. Not only were they able to study species in the bulk solution but also at the very surface of the electrodes. In their study of tetracyanoquinodimethane (TCNQ) (*2, 3*) they obtained Raman spectra of both TCNQ and its radical anion $TCNQ\cdot^-$. Whereas the electronic absorption spectrum of $TCNQ\cdot^-$ has little structure in the region from 15,000 to 18,000 $cm^{-1}$, the RR excitation profiles (plots of band intensity versus source frequency) showed great detail in this same region (see Fig. 4). Excitation profiles obtained from RR spectra show maxima whenever the denominator in the first term of eqn. (3) (recall that intensity is related to $\alpha$) passes through a minimum. This will occur whenever $\nu_0$ is equal to $\nu_{rv,gk}$ i.e. . . . whenever the exciting frequency corresponds to the energy of a pure electronic transition plus some multiple of an excited state vibrational quantum. It is most significant that those modes that are strongly enhanced will also be the modes that vibronically contribute to the electronic absorption band (*20*). The $TCNQ\cdot^-$ profiles, which are the most complete profiles obtained for any compound studied to date, contain 90 intensity points per 1000 wavenumbers. Resolution of these profiles revealed that substantial vibronic structure is hidden in the electronic absorption band throughout the region studied (see Fig. 4). Indeed at least five vibrational modes that are involved are identified and their

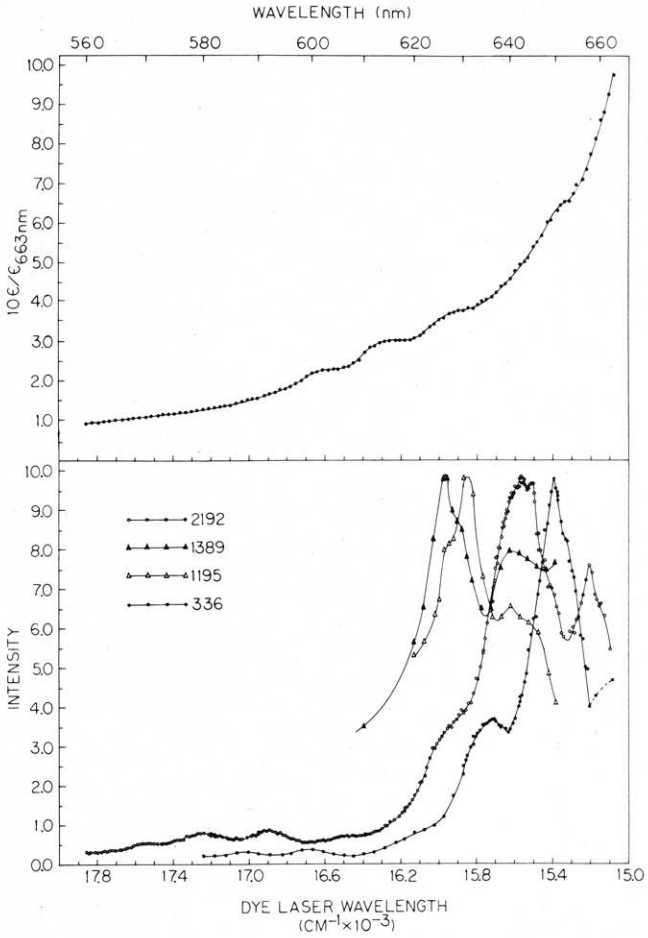


Figure 4. (A) Electronic absorption spectrum of $TCNQ\cdot^-$. (B) Resonance Raman excitation profiles of $\nu_2$ (2192 $cm^{-1}$), $\nu_4$ (1389 $cm^{-1}$), $\nu_5$ (1195 $cm^{-1}$) and $\nu_9$ (366 $cm^{-1}$). (Jeanmaire et al., Ref. (*3*))—reproduced by permission of the authors.

excited state frequencies assigned. These frequencies were then related to changes in calculated (CNDO/S) $\pi$ bond orders between the ground and excited states of $TCNQ\cdot^-$. Clearly some of the most exciting applications of RRS will be found in this new area.

## Conclusion

We have tried to present a simple introduction to the rapidly expanding field of RRS. To do this we have selected several applications which point up the sensitivity, selectivity and wide applicability of the RR effect. The article was not meant to be a comprehensive one but rather to establish a starting point from which the reader may proceed in many directions.


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