(7) E. Wilhelm and R. Battino, *J. Chem. Phys.*, **55**, 4012 (1971).
(8) D. S. Choi, M. S. Jhon, and H. Eyring, *J. Chem. Phys.*, **53**, 2608 (1970), and references therein.
(9) S. Abdulnur, Ph.D. dissertation, Yale University, 1966; *Diss. Abstr. B*, 4271 (1967).
(10) O. Sinanoglu and S. Abdulnur, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **24**, S-12 (1965).
(11) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
(12) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1964.
(13) H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.*, **32**, 119 (1960).
(14) R. C. Tolman, *J. Chem. Phys.*, **16**, 758 (1948); **17**, 118, 33 (1949).
(15) J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.*, **17**, 338 (1949); **18**, 991 (1950).
(16) F. P. Buff, *J. Chem. Phys.*, **23**, 419 (1955).
(17) S. Kondo, *J. Chem. Phys.*, **25**, 662 (1956).
(18) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", 3rd ed, Dover Publications, New York, N.Y., 1964.
(19) A. Beerbower, *J. Colloid Interface Sci.*, **35**, 126 (1971).
(20) H. Schonhorn, *J. Phys. Chem.*, **71**, 4578 (1967).
(21) E. Wilhelm and R. Battino, *J. Chem. Phys.*, **58**, 3561 (1973).
(22) "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology", Vol. IV., McGraw-Hill, New York, N.Y., 1928.
(23) E. Wilhelm, *J. Chem. Phys.*, **58**, 3558 (1973), and references therein.
(24) S. W. Mayor, *J. Phys. Chem.*, **67**, 2160 (1963).
(25) "Landolt-Bornstein Tabellen", band II, Teil 3, Springer-Verlag, Berlin, 1956.
(26) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, New York, N.Y., 1950.
(27) C. E. Weir, G. J. Piermarini, and S. Block, *J. Chem. Phys.*, **50**, 2089 (1969).
(28) N. Norman and H. Mathisen, *Acta Chem. Scand.*, **18**, 353 (1964).
(29) N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1747, 1755 (1961).
(30) D. André, R. Fourme, and K. Zechmeister, *Acta Crystallogr., Sect. B*, **28**, 2389 (1972).
(31) E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. R. Soc. London, Ser. A*, **247**, 1 (1958).
(32) R. Kahn, R. Fourme, D. André, and M. Renaud, *Acta Crystallogr., Sect. B*, **29**, 131 (1973).
(33) B. Post, R. S. Schwartz, and I. Frankuchen, *Acta Crystallogr.*, **5**, 372 (1952).
(34) B. Vonnegut and B. E. Warren, *J. Am. Chem. Soc.*, **58**, 2459 (1936).
(35) R. L. Collin, *Acta Crystallogr.*, **9**, 537 (1956).
(36) W. Biltz, A. Sapper, and E. Wunnenberg, *Anorg. Allgem. Chem.*, **203**, 277 (1932).
(37) D. N. Bol'shutkin, V. M. Gasan, and A. I. Prokhvatilov, *Zh. Strukt. Khim.*, **12**, 734 (1971).
(38) D. R. Sears and H. P. Klug, *J. Chem. Phys.*, **37**, 3002 (1962).
(39) D. L. Losee and R. O. Simmons, *Phys. Rev.*, **172**, 944 (1968), and references to earlier work.
(40) C. S. Barrett and L. Meyer, *Phys. Rev.*, **160**, 694 (1967).
(41) F. A. Mauer and H. S. Peiser, *Acta. Crystallogr.*, **12**, 247 (1959).
(42) J. D. H. Donnay, Ed., "Crystal Data Determinative Tables", 2nd ed, American Crystallography Association, 1963.
(43) A. J. Barlow, J. Lamb, and A. J. Matheson, *Proc. R. Soc. London, Ser. A*, **292**, 322 (1966).
(44) R. Fourme and M. Renaud, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **263**, 69 (1966).
(45) R. D. Burbank, *J. Am. Chem. Soc.*, **75**, 1211 (1953).
(46) S. G. Biswas, *Acta Crystallogr.*, **11**, 882 (1958).
(47) J. Trotter, *Acta Crystallogr.*, **12**, 884 (1959).
(48) L. A. Nisel'son, P. P. Pugachevich, T. D. Sokolova, and R. A. Bederdinov, *Zh. Neorg. Khim.*, **10**, 1297 (1965).
(49) S. Fuks and A. Bellemans, *Physica (Utrecht)*, **32**, 594 (1966).
(50) Least-squares fitting of values given by: A. J. Leadbetter and H. E. Thomas, *Trans. Faraday Soc.*, **61**, 10 (1965).
(51) F. B. Sprow and J. M. Prausnitz, *Trans. Faraday Soc.*, **62**, 1097 (1966).
(52) G. A. Cook, Ed., "Helium and the Rare Gases", Wiley, New York, N.Y., 1961.
(53) "Handbook of Chemistry and Physics", 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969–1970.
(54) Estimated from ΔH_v by $\Delta E_v \approx \Delta H_v - RT$ (see ref. 18, for example) based on data of: J. H. Colwell, E. K. Gill, and J. A. Morrison, *J. Chem. Phys.*, **40**, 2041 (1964).
(55) H. H. Chen, C. C. Lim, and R. A. Aziz, *J. Chem. Thermodyn.*, **7**, 191 (1975).
(56) Estimated as in ref 54 from ΔH_v data of: J. C. Mullins, W. T. Ziegler, and B. S. Kirk, *Adv. Cryog. Eng.*, **8**, 126 (1963).
(57) J. Lielmezs, *Thermochim. Acta*, **8**, 355 (1974).

Approximate Selection Rules for Resonance Raman Spectroscopy[1]

J. M. Friedman[2] and R. M. Hochstrasser*

Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174.

Received October 14, 1975

Abstract: The resonance Raman scattering tensor is developed and discussed. We contrast the resonance conditions that result in the enhancement of combinations and overtones of nontotally symmetric modes with those for the corresponding Raman fundamentals. By assuming a simplified model in the description of the resonant adiabatic state we are able to discuss the symmetry of the scattering tensor based on equilibrium molecular configurations. Within the framework of this model we show by symmetry that in certain commonly encountered limits, the resonance enhancement of antisymmetric combinations is very small whereas for others (equally allowed by rigorous symmetry rules) the enhancement is large and can be predicted from the intensities of the corresponding Raman fundamentals. Similar arguments are applied to the analysis of resonance Raman scattering involving Jahn–Teller active modes. Dispersion and interference effects are also considered in relation to the Raman excitation profile of nontotally symmetric vibrations. Finally we illustrate with results from ferrocytochrome-*c* how these principles can provide the information to make new vibrational assignments.

I. Introduction

With the increasing availability of powerful CW dye lasers it has become more feasible to record high resolution resonance Raman (RR) excitation profiles over rather extensive absorption regions. To exploit the informational content from such data it is necessary to incorporate a number of general principles governing resonance enhancements. Raman excitation profiles arising from resonances with strongly allowed transitions that display Franck-Condon progressions of totally symmetric modes are presently receiving considerable theoretical attention.[3] However, the principles for the Raman excitation of nontotally symmetric modes are not so thoroughly documented even though some of the essential points can be found in the literature.[4,5] Many of these principles are those that have been used by spectroscopists in relation to molecular fluorescence and hot band absorption spectroscopy. Although single vibronic level fluorescence and resonance Raman scattering are very nearly the same process, important differences both theoretical[6-10] and practical[7,11] do exist.

In single level fluorescence the contribution of the off-resonance molecular states is in general negligible compared with that of the resonant fluorescent quasi-stationary state. Molecular states not on resonance contribute primarily for the duration of the exciting pulse which in fluorescence decay experiments is generally much shorter than the fluorescence lifetime, or for the coherence time of the photons in a CW experiment. In practice it is only the resonant fluorescent state (or states) that is exposed by studies of spectra and lifetimes. The coherent superposition of molecular states that gives rise to observable resonance Raman will often contain a dominant resonant term but the off-resonance contributions do manifest themselves in the Raman excitation profiles[12-15] and in the energy dispersion of the Raman depolarization ratio.[15-17] The latter is an experimental quantity that results from both the coherence between the incident and Raman scattered photons and the temporal features of the resonance scattering event. Experimentally these off-resonance contributions are appreciable only if the energetically sharp Raman generating excitation is scanned through the energy region of the resonance. For the case where there is a dominant resonant contribution to the Raman scattering the selection rules governing the fluorescence and the Raman processes are very nearly identical, the difference between them being that the lifetime of the resonant molecular state (due to radiative and nonradiative effects) does not appear in a simple manner as broadening of the Raman spectra.[7,8]

It is the purpose of this paper to describe those principles and selection rules that govern the appearance in the RR spectra of the various harmonics of nontotally symmetric vibrational modes. As implied by the preceding discussion some of these principles are no different from those known for single vibronic level fluorescence while others are inherent to Raman-like transitions.

II. Scattering on to Combination and Overtone Bands

In this paper we examine the conditions under which there is resonance enhancement of Stokes Raman transitions to the higher harmonics (i.e., combinations and overtones) of ground state modes that correspond to Franck-Condon inactive or vibronically induced excited state modes. In addition we illustrate with results from ferrocytochrome-*c* how the higher harmonics can provide information necessary to make heretofore unmade symmetry assignments.

(1) The Resonance Raman Amplitude. We consider resonance with just one electronic state i, whose vibronic levels $|i; n_{\nu'}\rangle$ can undergo radiative transitions to one other electronic state, usually, but not necessarily, the ground state g with vibronic levels $|\mathrm{g}; n_{\nu''}\rangle$. The remaining levels assume the role of a quasi-continuum providing nonradiative decay channels for the relevant levels of $|i\rangle$ (i.e., we do not consider the so called intermediate coupling case). It has been shown rigorously[7] that for the case under consideration when monochromatic excitation is employed (or if $\gamma_{in_{\nu'}} \gg \gamma_{\text{photon}}$) the contribution to the $|\mathrm{g}; 0\rangle \rightarrow |\mathrm{g}; n_{\nu''}\rangle$ Stokes Raman amplitude from a resonance with given vibronic level $|i; n_{\nu'}\rangle$ is given by:

$$A_{\mathrm{g}0\rightarrow \mathrm{g}n_{\nu''}} = \frac{\langle n_{\nu''}; \mathrm{g}|e_i \cdot r|i; n_{\nu'}\rangle \langle n_{\nu'}; i|e_1 \cdot r|g; 0\rangle}{\epsilon(i; n_{\nu'}) - \epsilon_{\mathrm{p}} + (i/2)\gamma_{in_{\nu'}}} \quad (1)$$

where n_ν refers to the occupation number (number of quanta excited) for the νth mode. $\epsilon(i; n_\nu)$ is the stationary energy of the vibronic state $|i; n_\nu\rangle$, ϵ_{p} is h times the peak frequency of the incident light pulse, and $\gamma_{\mathrm{i}n_\nu}$ is the homogeneous half-width ($\gamma = \hbar/\tau$) of the vibronic level $|i; n_\nu\rangle$. The products of electric dipole matrix elements in eq 1 combine into the elements of the Raman amplitude scattering tensor, and in general they transform like a reducible representation of the symmetry point group of the molecule defined by some equilibrium nuclear configuration. In Albrecht's earlier treatment[4] of Raman scattering the Herzberg-Teller expansions were substituted into the Raman amplitude expression. In order to be able to use symmetry arguments it is convenient to consider the electronic part of the vibronic state as a superposition of basis electronic states $|i^0\rangle$ having energy $\epsilon_i{}^0$ all defined at a fixed nuclear configuration, the nuclear positional dependence of the adiabatic electronic state being in the expansion coefficients. It should be reemphasized[5] that *these basis states cannot be resonant states in a normal experiment.* They do not represent distinguishable states as far as normal light pulses are concerned.[18,7] In cases where this so-called Herzberg-Teller expansion is most useful, the ground and excited state geometries should not differ substantially and the expansion coefficients should be small. This latter restriction is achieved by excluding high-amplitude vibrations. We will consider a simplified expansion for the electronic states that involves linear nuclear normal mode (R_α) vibronic coupling between only three fixed nucleus electronic states:

$$|i\rangle = |i^0\rangle + \sum_\alpha [C_\alpha(i^0|j^0)|j^0\rangle + C_\alpha(i^0|k^0)|k^0\rangle] \quad (2)$$

We will further assume the electric dipole transition moments to satisfy $\mu_{\mathrm{g}j} \gg \mu_{\mathrm{g}i}$ and that the actual $|j\rangle$, $|i\rangle$, and $|k\rangle$ vibrational manifolds lie in quite different spectral regions such that isolated resonance conditions can be obtained. Normal modes of interest, labeled α, mix two equilibrium states to an extent determined by the magnitude of the linear vibronic coupling coefficients $C_\alpha(i^0|j^0)$. Ground state mixing is not considered explicitly.

Substitution of (2) into (1) results in the prediction that for the case $\mu_{\mathrm{g}i}{}^0 \equiv 0$ there are no resonance contributions from the 0–0 band ($|i; 0\rangle \leftarrow |\mathrm{g}; 0\rangle$) to the Raman scattering involving either the fundamentals or the combinations of the α modes. Resonance with the 0–1 transitions ($|i; 1_\alpha\rangle \leftarrow |\mathrm{g}; 0\rangle$), however, results in enhancements of the combinations of α modes (e.g., $|\mathrm{g}; 1_\alpha 1_{\alpha'}\rangle$). In the case $\mu_{\mathrm{g}i}{}^0 \neq 0$ resonance with the 0–0 can result in enhancements of the α-mode fundamentals ($|\mathrm{g}; 1_\alpha\rangle \leftarrow |\mathrm{g}; 0\rangle$) but not the higher harmonics.[31] When the resonance is with the 0–1 of a particular α mode then both the fundamental and combinations of the corresponding ground state mode are enhanced in the Raman spectra. It should be noted that one-to-one correspondence between excited and ground state α modes may not be evident if there is a significant Duchinsky effect.[19,20]

The mechanism for the resonance enhancement of the fundamental differs from that of the combinations and overtones in that the former involves a contribution from both the $|i^0\rangle$ and $|j^0\rangle$ component of the resonant state $|i\rangle$ whereas the combinations and overtones ($n' = 2$) occur exclusively through the $|j^0\rangle$ component. The ratio of the 0–1 resonance Raman intensity for the fundamental of a mode α to that for a combination of this mode with a mode α' is in most cases given approximately by the ratio of the 0–0 to 0–$1_{\alpha'}$ absorption intensity. (We are of course assuming that all modes are harmonic.)

(2) Symmetry Considerations for Combinations. As mentioned earlier the product of electric dipole matrix elements defines part of the second rank Raman scattering tensor for the transition. The group theoretical direct product of the coordinate representations for the two dipole moments is in general a reducible representation of the point group defined by the symmetry of the equilibrium configuration of the molecule. For example, if the representation for the x, y electric dipole moment components $\mu(x)$, $\mu(y)$ is degenerate then the direct square of the coordinate representation will reduce to the sum of three symmetric and one antisymmetric direct product irreducible representations. The Raman scattering amplitude tensor having symmetry $\Gamma(\mathrm{g}; 0) \otimes \Gamma(\mathrm{g}; n_{\nu''})$ can in general be expressed as the sum of three tensors: the isotropic or trace scattering tensor, the symmetric tensor, and the antisymmetric tensor. The latter two describe contributions to the Raman transition that behave like electric quadrupole and magnetic dipole (axial vector) transitions, respectively. The Raman transition probability consists of the square of the sum of these contributing tensors. Only one factor occurs for each choice of initial and final states. The various tensor components that can exist for various symmetry groups have been summarized most recently by McClain.[21]

We will consider Raman transitions involving two quanta of nontotally symmetric modes ($|g; 2_\alpha\rangle \leftarrow |g; 0\rangle$ are overtones; $|g; 1_\alpha 1_{\alpha'}\rangle \leftarrow |g; 0\rangle$ are combinations) in molecules having sufficiently high symmetry that the Raman transition probability can be simplified by group theory. The resonant states are assumed to be electronic states that are effectively degenerate in a first approximation since this case brings out many of the more interesting and immediately relevant features of RR scattering involving combinations and overtones of nontotally symmetric modes. Attention will be focused upon those Raman transitions whose Raman tensors are primarily antisymmetric. Antisymmetric vibrational scattering, which has only recently been observed,[22] involves a directional 90° rotation of the plane polarization of the incident radiation. For this to occur electric dipole allowed electronic configurations must be made accessible over the range of the molecular distortion.

When the resonant adiabatic electronic state is degenerate then the Raman scattering tensor for combinations and overtones of nontotally symmetric modes can have contributions from each of the tensor components isotropic, symmetric, and antisymmetric. The contribution of the antisymmetric part manifests itself in a value of the depolarization ratio greater than ¾ which tends to infinity as the other two tensor components go to zero. A further analysis in terms of nuclear coordinate fixed electronic states that compose the resonant adiabatic electronic state can provide information about the relative magnitudes of the contributing tensor types on the basis of symmetry.

For example, if the resonant adiabatic electronic state transforms according to the E representation of the D_4 point group, we can write it as a superposition of degenerate equilibrium electronic states vibronically mixed by normal modes (R_α) having symmetry species $E \otimes E = a_1 \oplus b_1 \oplus b_2 \oplus a_2$:

$$|E_{ia}\rangle = |E^0{}_{ia}\rangle + \sum_{\alpha,b,j} C_\alpha(E^0{}_{ia}|E^0{}_{jb})|E^0{}_{jb}\rangle \tag{3}$$

where E_{ia} is the ath component of the ith degenerate (E) state and $E^0{}_{ja}$ is the electronic wave function at the equilibrium symmetry.

There are three cases of higher harmonic scattering that we consider: (a) Stokes scattering involving combinations of modes that mix the ith state with exclusively *one* E state from the sum, say the jth. (b) Stokes scattering involving combinations of modes one of which mixes E states i and j and the other mixes i with k. (c) Anti-Stokes scattering in the Stokes region.

The first two cases involve combinations of those ground electronic state modes that correspond to the modes that are vibronically active in mixing degenerate equilibrium states. For a molecule having D_4 symmetry those vibronically active modes have symmetry a_1, a_2, and b (b_1, b_2). Thus the Raman scattering tensor for the transition $|g; 1_\alpha 1_{\alpha'}\rangle \leftarrow |g; 0\rangle$ can be isotropic, symmetric, or antisymmetric depending on whether the direct product of the component modes transforms as the a_1, b(b_1 or b_2), or a_2 representations, respectively. (Note that for the equilibrium states the vibronic symmetry is the product of an electronic and vibrational part.) As discussed in section II.1 the combinational scattering for these modes is enhanced by resonances with their 0–1 transitions and the incident and scattered radiation electric dipoles couple to the resonant adiabatic state via the vibronically mixed in nuclear coordinate fixed electronic states $E^0{}_j$ or $E^0{}_k$. When the two modes of the combination vibronically couple $E^0{}_{ia}$ to the same equilibrium basis state (case a) then the scattering tensors will be proportional to a linear combination of products of matrix elements for electric dipole transitions between the ground electronic state and the one mixed in state. More generally for this case the components of the amplitude factor A can be developed as:

$$A_{ab} = \sum_c \frac{\langle g; 0|er_a|E_{ic}; 1_\alpha\rangle\langle E_{ic}; 1_\alpha|er_b|g; 1_\alpha 1_{\alpha'}\rangle}{\epsilon(ic; 1_\alpha) - \hbar\omega + i(\gamma/2)} \tag{4}$$

Substitution of (3) into (4) and collecting terms using the case (a) restriction gives the amplitude in the form:

$$A_{ab} = \mu^0{}_{0j_a}\mu^0{}_{j0_b}T_{ab}(\alpha,\alpha') \tag{5}$$

with the following definitions, and a, b, . . . representing the components of the degeneracy (i.e., they label partner functions):

$$\mu^0{}_{0j_a} = \langle g 0|ea|E^0{}_{ja}\rangle \tag{6}$$

$$T_{ab} = C_{ij}(\alpha,\alpha') \sum_c \frac{\langle E^0{}_{ja}|V_\alpha|E^0{}_{ic}\rangle\langle E^0{}_{ic}|V_{\alpha'}|E^0{}_{jb}\rangle}{\epsilon(ic; 1_\alpha) - \hbar\omega + i(\gamma/2)} \tag{7}$$

with V_α representing a derivative of the potential $(\partial V/\partial R_\alpha)_0$.

$$C_{ij}(\alpha,\alpha') = \langle R_\alpha\rangle_{01}\langle R_{\alpha'}\rangle_{01}/(E^0{}_1 - E^0{}_j)^2 \tag{8}$$

When the i degeneracy is exact, the definition in (7) becomes:

$$T_{ab}(\alpha,\alpha') = \left[\frac{C_{ij}(\alpha,\alpha')}{\epsilon(i; 1_\alpha) - \hbar\omega + i(\gamma/2)}\right] \times \langle E^0{}_{ja}|V_\alpha V_{\alpha'}|E^0{}_{jb}\rangle \tag{9}$$

This result is to be contrasted with that obtained when the final state involves just one nontotally symmetric vibration. In that case (again assuming just one coupling state) one finds:

$$T_{ab}(\alpha) = \left[\frac{C_{ij}(\alpha)}{\epsilon(i;1_\alpha) - \hbar\omega + i(\gamma/2))}\right]\langle E^0{}_{ja}|V_\alpha|E^0{}_{ib}\rangle \tag{10}$$

where the new definitions are:

$$C_{ij}(\alpha) = \langle R_\alpha\rangle_{01}/(E^0{}_1 - E^0{}_j) \tag{11}$$

and

$$A_{ab} = \mu^0{}_{0j_a}\mu^0{}_{i_b0}T_{ab}(\alpha) \tag{12}$$

The crucial difference between (9) and (10) is that the set of components in (10) have an antisymmetric part whereas the tensor having the elements in (9) has no antisymmetric part. This result follows from group theory: The direct product space spanned by the four products $E^0{}_{ja}E^0{}_{ib}$ is four dimensional, such that there are four irreducible components. The direct product space spanned by the set of products $E^0{}_{ja}E^0{}_{jb}$ is only three dimensional such that only the bases of the symmetric direct product can occur.[32] Case (b) coupling involves two states so once again both the symmetric and antisymmetric parts of the scattering tensor can occur. The practical consequence of these results is that in case (a) situations antisymmetric tensor resonance Raman scattering will not appear onto combination bands even though the total symmetry of the vibrational state (i.e., the direct product of the vibrational species involved) is contained in the antisymmetric part of the direct product $E \otimes E$. The latter is the usual criterion for the appearance of antisymmetric tensor resonance enhanced scattering. In real situations where the present model is not exact the theory predicts only a small resonance enhancement for those combinations having the symmetry of the antisymmetric direct product compared with those that involve the symmetric part.[33]

If we are dealing with case (b) so that the α and α' modes couple different pairs of degenerate states with comparable efficiency then the antisymmetric combination scattering tensor clearly does not vanish and we can anticipate no marked abnormality for the intensity of the antisymmetric combinations. Similarly, in D_4, when the antisymmetric combination is composed of an a_2 and an a_1 mode, the antisymmetric tensor can vanish in our model if a_2 and a_1 couple the same pair of basis states (which is allowed by symmetry); however, if the a_1 mode is a Franck-Condon mode then the antisymmetric combination is indeed nonzero: This is easily demonstrated by a trivial extension of our model.

The same symmetry rules apply to Raman difference bands which initiate from a vibrationally excited ground state level $|g; 1_\alpha\rangle$ and terminate in another vibrational level $|g; 1_\beta\rangle$ that may be at higher energy (i.e., $h\nu_\alpha < h\nu_\beta$). Of course the intensity of any such Raman difference band critically depends upon the Boltzman factor for the initial state, $|g; 1_\alpha\rangle$. While the combinations under discussion require a 0–1 resonance state, these difference bands, case (c), require a 0–0 type resonant intermediate state and a different resonance energy denominator $[\epsilon(i; 0) - \hbar\omega - \epsilon(g; 1_\alpha) + (i\gamma/2)]$. It was previously suggested by us[5] that some of the already observed low-frequency peaks in the resonance Raman spectra of ferrocytochrome-*c* might be assigned as difference bands. Our subsequent Raman work[7,17] at liquid He temperature has shown that these bands are still present at low temperature and perhaps even enhanced with respect to 300 K, which proves our earlier suggestions to be incorrect. No one has yet reported these anti-Stokes bands in the Stokes region, but their identification will provide opportunity for an evaluation of the theoretical models.

The distinction between cases (a) and (b) for $\Gamma(\alpha) \otimes \Gamma(\alpha') = a_2$ can be made experimentally when the fundamentals ν_α and $\nu_{\alpha'}$ each exhibit significant scattering enhancement as a result of 0–0 and 0–1 resonance. For combination scattering we expect a similar 0–1 enhancement for the combinations of ν_α and $\nu_{\alpha'}$; however, for case (a) but not for case (b) there is predicted from our model a marked decrease in the Raman intensity relative to qualitative expectations based on knowledge of the scattering intensities for fundamentals and absorption intensities for 0–0 and 0–1 transitions.

When the molecular symmetry is rigorously D_4, antisymmetric scattering manifests itself experimentally via an infinite depolarization ratio. Deviations from *x*, *y* equivalence (e.g., splitting of the degeneracy) will result in a scattering tensor that is no longer purely antisymmetric but contains a "symmetric" part (in the basis of the higher symmetry group) which also displays an excitation energy dispersion. The case (a) antisymmetric combinational scattering will no longer be rigorously zero as can be seen from (7) when the energy denominators in the difference $(T_{ab} - T_{ba})$ are no longer identical. Since there is an excitation energy dependent symmetric and antisymmetric contribution (again in the basis of the higher symmetry group), the polarization ratio as well as the intensity will display an energy dispersion.

The foregoing considerations suggest other symmetry guides for scattering processes, in particular for the case of the Jahn–Teller effect. The Jahn–Teller effect is brought about by those nuclear displacements that transform like irreducible representations belonging in the symmetric part of the direct square of the degenerate representation. The anomalously polarized Raman transitions involve those vibrations from the antisymmetric direct square of the coordinate representation. Thus there are cases when antisymmetric tensor resonance scattering and the Jahn–Teller effect are mutually exclusive. If a Jahn–Teller active state can be observed optically (i.e., if the symmetry is that of the degenerate coordinate representation) then antisymmetric tensor scattering should not be enhanced unless by vibronic coupling with some other state. In a recent paper[23] describing the resonance Raman spectrum of the iridium hexachloride ion a relationship between the appearance of an anomalously polarized Raman peak and a Jahn–Teller effect in the resonant excited state was suggested. We can suggest on the basis of the foregoing that the appearance of an anomalously polarized vibrational Raman transition is more likely to signal vibronic coupling between nuclear coordinate fixed electronic configurations whose species direct products contain an antisymmetric component.

(3) **Raman Excitation Profile.** Because of the different mechanisms of resonance enhancement of fundamentals and combinations in Raman scattering we expect different excitations profiles in the two cases. Raman fundamentals which derive intensity from both the 0–0 and 0–1 resonances can be expected to display an excitation profile that peaks close to the 0–0 and 0–1 transitions for the appropriate mode, provided the energy separation between the two absorption regions exceeds one-half the half-widths. In the excitation profiles, symmetry and energy dependent deviations from the simple absorption profiles are expected as a result of quantum interferences between the 0–0 and 0–1 contributions[14,15] and, if the resonant electronic state is nearly degenerate, between the *x* and *y* components of the resonant and near resonant levels.[17] The combinations on the other hand can be expected to present a Raman excitation profile that primarily follows the absorption profile of the contributing 0–1 transitions with modifications due to interference and half-width considerations ($|\epsilon(i;|\epsilon(i;1_\alpha) - \epsilon(i;1_{\alpha'})| > (\gamma/2)$ for resolution of the two 0, 1 absorptions). Because a relatively small fraction of the total number of vibronic levels contribute to any one excitation profile involving vibronically active modes it is possible thereby to map out structure in absorption spectra that are diffuse and structureless as a result of level congestion. Of course if there is a complete absence of structure due to lifetime broadening ($\gamma/2 > \Delta\epsilon$), then the profiles presumably will not display any additional underlying vibrational structure.

We now illustrate how most of these principles can be applied in the relatively well studied resonance Raman spectra of cytochrome-*c*.

III. Ferrocytochrome-*c* Combination and Overtone Scattering:

Excitation of ferrocytochrome-*c* with visible laser radiation generates resonance enhanced Raman spectra[5,7,14,16,24-29] that involve those ground state modes that correspond to vibronically active modes of the resonant excited state. Modes of the four symmetry types a_1, a_2, b_1, and b_2 (assuming D_4 symmetry for the porphryin chromophore) are permitted in the spectrum along with e modes due to vibronic coupling with A_2 states; the scattering tensor either transforms as an antisymmetric representation of the point group of the molecule or it contains an antisymmetric component (which can be excitation energy dependent). For vibrational Raman (as opposed to electronic Raman) scattering, the presence of an antisymmetric scattering tensor is associated with either actual degeneracy or an effective degeneracy due to the particular choice of excitation energy. Typically one would have $|Q_x\rangle$ and $|Q_y\rangle$ electronic states (corresponding to the components of the Q or α band) and each of these adiabatic states can be expressed as a superposition of the respective equilibrium components $|Q_x{}^0\rangle$ and $|Q_y{}^0\rangle$ with the equilibrium states $|S_y{}^0\rangle$ and $|S_x{}^0\rangle$ (corresponding to the components of the Soret band). For the combinations, the antisymmetric contribution to the scattering tensor transforms as the antisymmetric direct product involving the components $|S_x{}^0\rangle$ and $|S_y{}^0\rangle$. For those point groups where there is *x*, *y* equivalence it is relatively straightforward to distinguish between a_2 and b modes on the basis of Raman polarizations of the fundamentals but one cannot readily distinguish between the b_1 and b_2 fundamentals both having a depolarization ratio (ζ) of 0.75. We report spectra below which, when analyzed according to the principles enumerated in the prior sections, results in the model dependent distinction between b_1 and b_2 modes.[34]

In particular we focus on the resonance enhanced 752 cm^{-1} ground state b mode ($\zeta = 3/4$). We observe that for this mode at 0-1 resonance there is significant enhancement of the fundamental (752 cm^{-1}), the overtone (2×752 cm^{-1}), and the various combinations with other vibronically active modes (Figure 1). The symmetry of the possible combinations straightforwardly derived from group theory for D_4 symmetry are: $b_1 \otimes b_1 = b_2 \otimes b_2 = a_1$; $b_1 \otimes b_2 = a_2$, $b_1 \otimes a_2 = b_2$; and $b_2 \otimes a_2 = b_1$. In a first approximation the resonant adiabatic electronic state $|Q\rangle$ is degenerate and we can expect $b_2 \otimes b_1 = a_2$ antisymmetric combination scattering to be diminished or absent from the spectra to the extent that the resonance state has equal admixtures of x, y components. Since it is known that the x and y intensities are quite closely equal we predict that the overtone of 752 cm^{-1} (having a_1 total symmetry), combinations of 752 cm^{-1} with b modes of the same symmetry (a_1 total symmetry), and combinations of 752 cm^{-1} with a_2 modes (b total symmetry) will be distinctly apparent in the spectrum while combinations of the 752-cm^{-1} mode with b modes of different b symmetry (having a_2 total symmetry) should be weak in comparison. Examination of Figure 1 reveals that most of the observed b mode combinations with the 752-cm^{-1} mode are both intense and polarized consistent with these modes having the same b symmetry assignment. The intensity of the combination of 752 with the 1367-cm^{-1} b mode[35] is extremely weak in comparison and the value of ζ, although difficult to measure very accurately, is between 0.75 and unity (i.e., ≥ 0.75). These results are suggestive of the 1367-cm^{-1} b mode being of different symmetry than the 752-cm^{-1} b mode.

The actual assignment of the b modes requires a further appreciation of the resonance Raman scattering mechanism. It is known that the metalloporphyrins frequently deviate from D_4 equilibrium symmetry. Whereas for the D_4 point group the scattering tensors of a_2 symmetry ($|g; 1_{a_2}\rangle \leftarrow |g; 0\rangle$ for example) and of b_2 symmetry ($|g; 1_{b_2}\rangle \leftarrow |g; 0\rangle$) are purely antisymmetric and symmetric, respectively. For lower symmetries the tensor representations that correlate with a_2 and b_2 in the D_4 point group contain an excitation energy dependent symmetric and antisymmetric component, respectively. The various symmetric and antisymmetric contributions to the scattering will exhibit energy dispersions provided the half-widths of the contributing levels are not excessively large. With the 5308-Å excitation which is situated between the Q_0 (α band) and Q_v (β band) transition regions we have $(\epsilon_{Q_0} - \epsilon_p) \approx -(\epsilon_{Q_v} - \epsilon_p)$. Thus with respect to the higher frequency modes (>1000 cm^{-1}) a resonant state is generated that is a superposition of nearly equivalent contributions from the Q_0 (or 0-0) and the Q_v (or 0-1) x and y components. It is in this excitation regime that we expect to see and do see manifestations of quantum interferences between the two groups of resonances. A germane aspect of this interference phenomenon is that the symmetric component of the Raman tensor for fundamentals destructively interferes, while the corresponding antisymmetric component either constructively interferes or remains relatively constant without a significant dispersion. Therefore for b_2 modes, *but not b_1* modes, we can anticipate seeing a ζ in excess of ¾ in this excitation region. As reported previously[16] we also observe a $\zeta > 3/4$ for the 1367-cm^{-1} mode but not for the other b modes for this excitation. This result strongly suggests that the 1367-cm^{-1} mode is a b_2 mode while the other b modes including the 752-cm^{-1} mode are of species b_1. This observation that combinations of the 752-cm^{-1} mode with various a_2 modes results in a Raman peak having values of ζ near unity is also consistent with a b_1 assignment for the 752-cm^{-1} mode. The reason is that the resulting b_2 combination ($a_2 \otimes b_1 = b_2$) will have an antisymmetric contribution for the known deviation from the D_4 symmetry.

Recently Stein, Burke, and Spiro[30] have reported a preliminary normal mode analysis of the porphyrin chromophore in heme-proteins from which they suggested assignments for the various b modes: Our experimentally determined assignments based on the simple model set down here are consistent with these results.

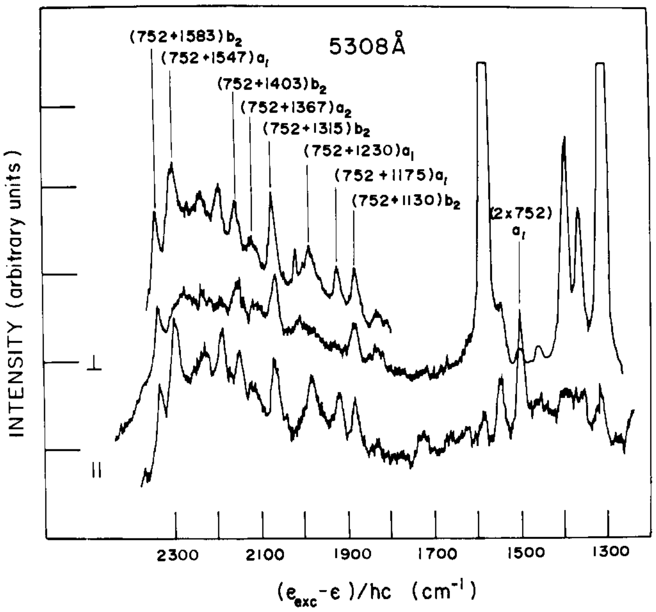

Figure 1. The 5308 Å (150 mW) RR spectrum of ferrocytochrome-*c* is shown. The top spectrum was not analyzed with a polarizer while the bottom two spectra are the perpendicular and parallel contributions to the scattered light. Experimental conditions as in ref 5. The broad background seen here is primarily the 1-0 relaxed fluorescence emission from ferrocytochrome-*c*.[14]

Conclusion

In this paper we examine some of the consequences to the resonance Raman spectrum of adopting a model for resonant adiabatic vibronic states that consist of describing the nuclear displacement averaged electronic configuration in terms of nuclear coordinate fixed electronic configurations that are coupled via linear displacements of the normal modes of the molecule from their equilibrium position. This model is specially convenient since we can assign specific symmetries to the various electronic configurations at the equilibrium geometry. With regard to those normal modes that are involved in the above described coupling the following selection rules are obtained.

1. Scattering onto the fundamentals can be enhanced with 0-0 and 0-1 resonances.

2. Scattering onto the combinations and overtones of these vibronically active modes can be enhanced only with 0-1 resonances.

3. Resonance enhancement of the fundamentals occurs through radiative coupling to two different fixed geometry electronic configurational components of the resonant electronic state.

4. Resonance enhancement of combinations and overtones of these modes occurs through radiative coupling to the same two fixed geometry electronic configurational components of the resonant adiabatic electronic state.

5. As a consequence of (3) and (4) the fundamentals but not the combinations of vibronically active modes can have significant antisymmetric scattering tensors when the coupled electronic configurations are effectively degenerate.

6. The appearance in the scattered spectrum of manifestations of an antisymmetric tensor is likely to signal vibronic coupling of two *different* fixed geometry electronic configurations and consequently is not an indication of or a manifestation of a first-order Jahn-Teller effect in the resonant vibronic state.

7. The resonance Raman excitation profile for the funda-

mentals of vibronically active modes can be expected to be modified by interference effects between the 0-0 and 0-1 resonances. These interference effects are expected to be very different for modes of different symmetries.[14]

8. As a consequence of (7) the depolarization ratio can be expected to display a dispersion for some modes over the 0-0 and 0-1 resonance regions when the coupled electronic configurations are *nearly* degenerate, provided the homogeneous widths are not too large.

References and Notes

(1) This research was supported in part by a PHS Grant GM12592 and in part by the LRSM through the NSF/MRL program.
(2) Recipient of the MSTP grant of NIH.
(3) (a) M. Mengardi, W. S. Siebrand, D. Van Labeke, and M. Jacon, *Chem. Phys. Lett.*, **31**, 208 (1975); (b) M. Mengardi and W. S. Siebrand, *J. Chem. Phys.*, **62**, 1074 (1975); (c) D. Van Labeke and M. Jacon, *Chem. Phys. Lett.*, **34**, 160 (1975).
(4) A. C. Albrecht, *J. Chem. Phys.*, **34**, 1476 (1961).
(5) J. M. Friedman and R. M. Hochstrasser, *Chem. Phys.*, **1**, 457 (1973).
(6) J. O. Berg, C. A. Langhoff, and G. W. Robinson, *Chem. Phys. Lett.*, **29**, 305 (1974).
(7) J. M. Friedman and R. M. Hochstrasser, *Chem. Phys.*, **6**, 155 (1974).
(8) S. Mukamel and J. Jortner, *J. Chem. Phys.*, **62**, 3609 (1975).
(9) A. Szoke and E. Courtens, *Phys. Rev. Lett.*, **34**, 1053 (1975).
(10) R. C. Hilborn, *Chem. Phys. Lett.*, **32**, 76 (1975).
(11) P. F. Williams, D. L. Rousseau, and S. H. Dworetsky, *Phys. Rev. Lett.*, **32**, 196 (1974).
(12) M. Jacon, M. Berjot, and L. Bernard, *Opt. Commun.*, **4**, 117 (1971).
(13) L. Rimai, M. E. Heyde, H. C. Hiller, and D. Gill, *Chem. Phys. Lett.*, **10**, 207 (1971).
(14) J. M. Friedman and R. M. Hochstrasser, *Chem. Phys. Lett.*, **32**, 414 (1975).
(15) O. S. Mortensen, *Chem. Phys. Lett.*, **30**, 406 (1975).
(16) D. W. Collins, D. B. Fitchen, and A. Lewis, *J. Chem. Phys.*, **59**, 5714 (1975).
(17) J. M. Friedman, Ph.D. Dissertation, University of Pennsylvania, 1975.
(18) R. Lefebre, *Chem. Phys. Lett.*, **8**, 306 (1971).
(19) G. J. Small, *J. Chem. Phys.*, **54**, 3300 (1971).
(20) B. Sharf and B. Hornig, *Chem. Phys. Lett.*, **7**, 132 (1970).
(21) W. M. McClain, *J. Chem. Phys.*, **55**, 2789 (1971).
(22) First reported by: T. G. Spiro and T. C. Strekas, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2622 (1972).
(23) H. Hamaguchi, I. Harada, and T. S. Shimanouchi, *Chem. Phys. Lett.*, **32**, 103 (1975).
(24) T. C. Strekas and T. G. Spiro, *Biochim. Biophys. Acta*, **278**, 188 (1972).
(25) H. Brunner, *Biochem. Biophys. Res. Commun.*, **51**, 888 (1975).
(26) L. A. Nafie, M. Pezolet, and W. L. Peticolas, *Chem. Phys. Lett.*, **20**, 563 (1973).
(27) M. Pezolet, L. A. Nafie, and W. L. Peticolas, *J. Raman Spectrosc.*, **1**, 455 (1973).
(28) J. Nestor and T. G. Spiro, *J. Raman Spectrosc.*, **1**, 455 (1973).
(29) T. G. Spiro and T. C. Strekas, *J. Am. Chem. Soc.*, **96**, 338 (1974).
(30) P. Stein, J. M. Burke, and T. G. Spiro, *J. Am. Chem. Soc.*, **97**, 2304 (1975).
(31) The quadratic terms (in R_α^2, $R_\alpha R_\alpha'$) and higher order terms omitted in eq 2 can give rise to the appearance of overtones and combinations only for a 0-0 resonance. These higher order corrections are in most instances expected to contribute to the scattering pattern to a significantly smaller degree than the first order terms. Recently one of the authors (J.M.F.) in conjunction with D. Rousseau recorded the RR spectrum of ferrocytochrome-*c* at ~5 K with the excitation exactly on resonance with the peak of the α band (0-0). While the spectrum displays the markedly enhanced fundamentals of the vibronically active modes there is no evidence in the spectrum of the combinations and overtones of these modes that appear for β band (0-1) resonances (see ref 5) suggesting that the linear approximation is certainly valid in that case.
(32) To obtain the closure relation in eq 9 we are making the assumption that ϵ_i^0 is the only equilibrium configuration electronic state that couples to ϵ_j^0 via V_α and $V_{\alpha'}$.
(33) Equations 10-12 are not equivalent to eq 1 of ref 26. The treatment leading to eq 10-12 involves resonance with a single adiabatic vibronic state, and therefore, there is only one resonance denominator in the scattering amplitude. The energies of the basis states, $\epsilon^0{}_i\epsilon^0{}_j$, and their differences *do not contribute to any resonance profile*. They are not readily related to the energies of the observed absorption peaks since they are associated with very large energy uncertainties (based on lifetimes) and energy corrections due to off diagonal elements in the scattering matrix. In our expressions they are constants resulting from treating the resonant state as an electronic configuration averaged over the many periods motion of the nuclei that occur during the photon molecular interaction. Detailed reasons for choosing the resonant state to be an adiabatic state were given in ref 7. In our model, the predictions as to which modes and which harmonics are expected to be enhanced are based exclusively on the numerator of the scattering amplitude when considering a single resonance or bunch of resonances, i.e., Q_0 or Q_v band. In marked contrast to ref 26 we do not expect a weaker resonance with the Q_0 band since the resonance denominators are expected to be very nearly the same in our model. Differences are expected if one takes into account nonadiabatic contributions to Q_0 and Q_v from S_v and S_0, respectively.

The symmetry arguments used by Pezolet, Nafie and Peticolas[26] do not imply the symmetry arguments we make in this paper since they specifically stated that both mixing and nonmixing processes yield the same selection rule, i.e., $\Gamma_\epsilon \times \Gamma_\epsilon$. Neither do these authors present a discussion of the mechanism or selection rules for scattering onto the higher harmonics of the nontotally symmetric modes.
(34) The reason that for certain small deviations from D_4 symmetry the b_2 mode fundamentals but not the b_1 mode fundamentals can have scattering tensors with an antisymmetric component is that the XY and YX tensor elements for b_2 are then unequal and it is possible to write their scattering amplitude tensor as follows:

$$\begin{pmatrix} 0 & XY & 0 \\ YX & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & \zeta+\eta & 0 \\ \zeta-\eta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & \zeta & 0 \\ \zeta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & \eta & 0 \\ -\eta & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

For the b_1 modes there may be no off diagonal tensor elements introduced by certain distortions and no antisymmetric part. As discussed in ref 14 and 17 the result of having both the 0-0 and 0-1 transitions contributing to the scattering process for the a_2, b_1 and b_2 (in D_4) fundamentals results in constructive interference for the antisymmetric component in the resonance regime *between* the 0-0 and 0-1 with concomitant destructive interference for the symmetric component. The reverse pattern occurs outside that energy regime. Consequently for deviations from *x*, *y* equivalence the depolarization ratio for the b_2 (D_4) mode fundamentals can display maxima of greater than 0.75 in the resonance region between the 0-0 and the appropriate 0-1.
(35) There is also a 1362-cm^{-1} a_1 mode in this region of the spectrum but it becomes enhanced via a Franck-Condon mechanism involving resonance with either the adiabatic states giving rise to the intense Soret absorption or via the nonadiabatic state between the Q_v band and the Soret.[5]