spectrum can be further resolved is clearly demonstrated experimentally.

The necessity of using a continuously tunable laser with as broad a tuning range as possible for the collection of RR excitation spectra (profiles) is illustrated here. Only in situations where the vibrational levels of the resonant excited state merge into a band of strongly overlapping levels to produce very broad RR excitation spectra will it be possible to obtain other than qualitative data using the coarsely and irregularly spaced lines of a multiple line, fixed frequency laser. Use of this type of laser exclusively to study systems in which the vibronic structure is either partially or fully resolved in the electronic absorption spectrum will produce, at best, an incomplete picture of the excitation spectra.

An assignment of the ν_2, ν_4, ν_5, and ν_9 RR excitation spectra of TCNQ$\cdot^-$ produced by $^2B_{3g} \rightarrow {}^2B_{1u}{}^{(1)}$ excitation was carried out. From this assignment it was possible to obtain the frequencies for the two modes most sensitive to electronic structure, ν_2' and ν_4', as well as the frequencies for the structure insensitive modes, ν_3', ν_5', and ν_9', in the $^2B_{1u}{}^{(1)}$ excited state. A qualitative correlation was obtained between CNDO/S calculated π bond order changes and experimental frequency changes for the optical and electron transfer induced electronic structure changes: TCNQ$\cdot^-(^2B_{3g}) + h\nu_0 \rightarrow$ TCNQ$\cdot^-(^2B_{1u}{}^{(1)})$ and TCNQ$\cdot^-(^2B_{3g}) + e^- \rightarrow$ TCNQ$^{2-}(^1A_g)$.

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The Relation of Heat of Vaporization to Surface Tension for Liquids of Nonpolar Spherical Molecules

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Abstract: A relation (eq 6a) between the energy of vaporization and the enthalpy part of surface tension is derived by considering the energy needed to vaporize a molecule from the liquid as equal to that required to create a molecular size spherical cavity within it. It is shown to apply for a variety of nonpolar and polar liquids. Assuming the applicability of macroscopic surface tension values to such dimensions, the radius of the cavity is shown to be that of a hard sphere in a Lennard-Jones 12-6 potential, $\sigma/2$. The relation accounts for Stefan's formula, the empirical relation first obtained by Hildebrand and Scott between surface tension and energy of vaporization, and the negative variation of σ with temperature. A method for obtaining reasonably good estimates of σ from liquid densities is also presented.

I. Introduction

The heat of vaporization of a liquid and its surface tension are macroscopic quantities that reflect the intermolecular forces present in the liquid. The search for a relation between them dates back to the latter part of the 19th century.[1] Such a relation may be derived from first principles through a statistical mechanical treatment of the liquid as a whole.[2] Alternatively, one may achieve this by focusing attention on a single molecule in a cavity in a liquid continuum, as will be shown in the present work. Using such an approach, Stefan in

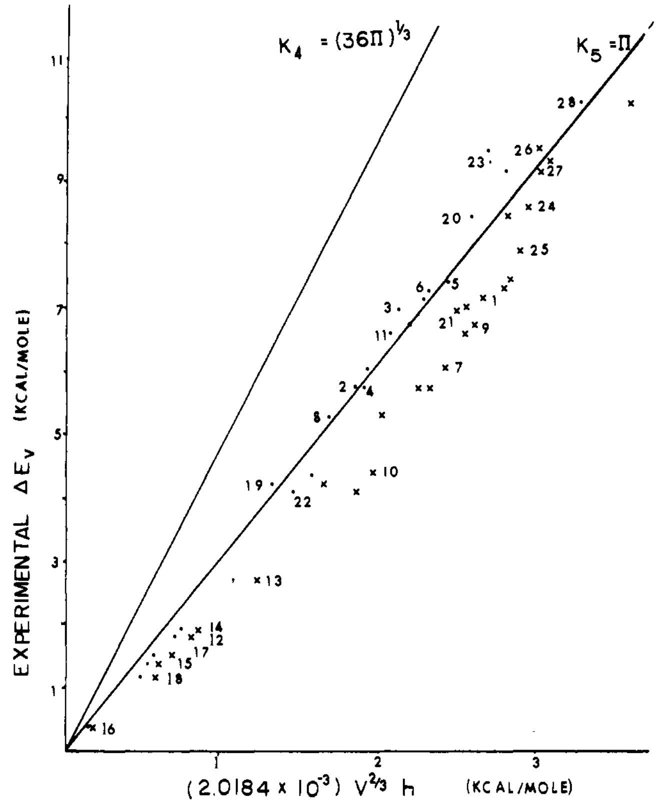

Figure 1. The experimental ΔE_v vs. the bracketed term on the rhs of eq 7. (●) and (X) refer to the values obtained for this term using V_0 and V, respectively. The numbers for the liquids are those in Table I. A (●) and a (X) on the same horizontal line refer to the same liquid.

1896 proposed that the work necessary to bring a molecule from the interior of the liquid to the surface is half that needed to vaporize it.[2,3]

The cavity picture has proved to be very useful in solution theory,[4-8] particularly when considering the effect of solvent on the properties of large biological systems,[9,10] following the pioneering work of Uhlig[4] in 1937. Uhlig perceived the solution process as consisting of two steps. In the first step one creates a cavity in the liquid. In the second, one places the solute in it and switches on its interaction with the solvent continuum. The size of the cavity and the applicability of macroscopic surface tension values for such microscopic dimensions are still open questions.[8] The present work investigates the implications regarding the size of the cavity if one assumes the macroscopic surface tension to hold for these dimensions.

II. Theory

The energy of vaporization per molecule, e_v, may be thought of as that energy needed to remove a molecule from the interior of the liquid to the vapor phase (the ratio of the number of molecules on the six faces of a cube to the number in the interior of the cube for a mole of liquid is $\sim 10^{-7}$). This hypothetical process results in the creation of a cavity inside the liquid if the volume of the latter is held constant.

e_v may be split up in the following manner:

$$e_v = e_i^{v} + e_c^{l} + \sum_k (e_k^{v} - e_k^{l}) \qquad (1)$$

where e_i^v is the energy of interaction of the molecule in the vapor phase and e_c^l is the energy needed to create the cavity in the liquid. The last term takes into account any differences in the energies of the various degrees of freedom of the removed molecule between the two phases. For liquids of nonpolar spherical molecules at ordinary temperatures and pressures, the first and last terms in eq 1 are usually negligible resulting in

$$e_v \cong e_c^{l} \qquad (2)$$

The energy needed to create a macroscopic spherical cavity of radius r in a liquid is:

$$e_c = 4\pi r^2 h \equiv 4\pi r^2 \left(\gamma - T\frac{d\gamma}{dT}\right) \qquad (3)$$

where γ is the surface tension (a free-energy term) and h is the enthalpy part of it (calculated from the term in parentheses). If the macroscopic γ and h are assumed to apply to the molecular size cavity considered here, the problem reduces to finding the appropriate r to be used in eq 3.

r may be obtained using the Onsager approximation[11] used in connection with the reaction field approach to molecular interactions in liquids, namely

$$[3V/4\pi N]^{1/3} = r \qquad (4)$$

in which V is the molar volume of the liquid and N is Avogadro's number.

One may also picture the liquid as divided into cubes each containing a spherical molecule. If one assumes the molecules to have such "effective" radii for them to touch one another, then the side of the cube would correspond to the diameter of such a sphere, or

$$\tfrac{1}{2}(V/N)^{1/3} = r \qquad (5)$$

For nonstructured liquids of the type considered here, the molar volume and hence the radius of the effective sphere will increase with temperature. By using for V in eq 5 values obtained at temperatures approaching 0 K from direct density measurements or low-temperature x-ray studies, one gets closer estimates to the physical radii of the molecules. Such a V is referred to henceforth as V_0.

Substituting eq 4 or 5 into eq 3 and 2 leads to:

$$e_v/(V/N)^{2/3}h = K_{4,5} \qquad (6)$$
$$K_4 = (36\pi)^{1/3};\ K_5 = \pi$$

where the constants K_4 and K_5 correspond to those using the approximations of eq 4 and 5, respectively. For $\Delta E_v = Ne_v$ in kcal/mol, V in cm^3/mol and h in ergs/cm^2, eq 6 becomes

$$\Delta E_v = K_{4,5}(2.0184 \times 10^{-3} V^{2/3} h) \qquad (7)$$

III. Results

Figure 1 shows a plot of the experimental ΔE_v versus the bracketed quantity on the rhs of eq 7 using both V and V_0 values for a variety of nonpolar liquids as well as some polar ones. The points are seen to be much more compatible with the present model of slope K_5 than with the Onsager model of slope K_4. The points obtained using the low-temperature V_0 values lie closer to the K_5 line (almost coinciding with it in many cases as in: CCl_4, *n*-pentane, ethyl ether, benzene, CS_2, SO_2, Br_2) than those using liquid V values, except for liquids like chlorobenzene, *m*-xylene, and *n*-octane where the situation is reversed. Upon rotational averaging, the molecules of these latter liquids generate ellipsoids deviating appreciably from spherical symmetry.

Table I compares the experimental ΔE_v values to the calculated ones using eq 5 and 7 and both V and V_0. With the exception of the cryogenic liquids, one may predict ΔE_v(exptl) to within 10% by using V_0 values, save for the three liquids previously mentioned where one must use their V values. For the cryogenic liquids the calculated ΔE_v values using V_0 are consistently larger than the experimental ones, although still within 13 to 26% of them.

Table I. Comparison of Experimental Heats of Vaporization with Those Calculated by (7) with $K_5 = \pi$[a]

Liquid	$V_0(T)$,[b] cm^3/(mol °K)	h,[c] ergs/cm^2	(h/γ)[c]	V_0/V[d]	ΔE_v(calcd),[e] kcal/mol	ΔE_v(exptl)(T),[f] kcal/(mol °K)
1. CCl_4	76.91 (h.p.)^{27}	61.94	2.315	0.8596	7.10 (8.26)	7.17
2. n-C_5H_{12}	81.99 (128)^{28}	48.25	3.016	0.7972	5.77 (7.24)	5.77
3. n-C_6H_{14}	97.93 (158)^{29}	48.89	2.657	0.8249	6.59 (7.98)	7.03
4. Ethyl ether	77.86 (128)^{30}	50.13	2.949	0.8251	5.80 (7.02)	5.75
5. C_6H_6	70.12 (78)^{31}	69.94	2.420	0.8540	7.54 (8.83)	7.45
6. Cyclohexane	81.87 (115)^{32}	60.18	2.407	0.8309	7.20 (8.66)	7.33
7. CS_2	42.66 (h.p.)^{27}	77.25	2.384	0.7941	5.98 (7.53)	6.1
8. SO_2	33.23 (77)^{33}	79.71	2.807	0.8292*	5.22 (6.30)	5.32 (263)
9. Br_2	38.69 (20)^{34}	93.09	2.243^{22}	0.8319*	6.75 (8.12)	6.75
10. Cl_2	33.45 (88)^{35}	74.0	2.824	0.8086*	4.87 (6.02)	4.42 (239)
11. $SiCl_4$	83.1 (0)^{36}	52.74	2.769^{48}	0.8053*	6.37 (7.91)	6.64
12. CH_4	30.56 (11)^{37}	34.90	2.296^{49}	0.8649*	2.16 (2.50)	1.84 (100)^{54}
13. Xe	34.72 (0)^{38}	49.39	2.655^{50}	0.8671*	3.33 (3.84)	2.72 (163)^{55}
14. Kr	27.10 (4)^{39}	40.58	2.547^{49}	0.8596*	2.32 (2.70)	1.95 (118)^{55}
15. A	22.56 (4)^{39}	31.93	2.445^{51}	0.8658*	1.62 (1.87)	1.40 (85)^{55}
16. Ne	13.39 (3)^{39}	13.43	2.821^{52}	0.8528*	0.48 (0.56)	0.41 (27)
17. O_2	20.91 (23)^{40}	36.34	2.236^{51}	0.8231*	1.75 (2.12)	1.55 (80)^{56}
18. N_2	27.29 (l.h.)^{41}	26.05	2.944^{51}	0.8472*	1.50 (1.77)	1.19 (77.3)^{54}
19. NH_3	19.78 (77)^{42}	88.04	4.002	0.7935^{53}	4.08 (5.15)	4.25^{57}
20. Toluene	93.01 (160)^{43}	61.53	2.167	0.9325	8.01 (8.75)	8.48
21. $CHCl_3$	62.50 (185)^{44}	66.19	2.433	0.8471	6.61 (7.80)	7.0
22. CH_3Cl	37.82 (148)^{45}	63.10	3.895	0.7802^{53}	4.51 (5.78)	4.14
23. n-C_8H_{18}	133.1 (203)^{29}	50.79	2.333^{26}	0.8752	8.40 (9.60)	9.35
24. Dioxane	u	74.59	2.223		(9.16)	8.6
25. Methylcyclohexane	u	56.05	2.355		(9.01)	7.89
26. m-Xylene	103.07 (93)^{42}	59.70	2.085^{26}	0.8896	8.32 (9.36)	9.53
27. C_6H_5Cl	91.89 (93)^{46}	67.29	2.022^{26}	0.9342	8.69 (9.30)	9.21
28. Nitrobenzene	89.86 (243)^{47}	80.25	1.828^{22}	0.9130*	10.21 (11.18)	10.3

[a] The calculated ΔE_v values and their constituent γ, h, and V values are at the same temperatures as the experimental ones in those cases where the temperature is indicated within parentheses in the last column. Otherwise they are at 20 °C while ΔE_v(exptl) is at 25 °C. [b] h.p. ≡ high pressure data; l.h. ≡ liquid hydrogen temperature; u ≡ data unavailable. [c] Except where indicated, the γ values used here are obtained from ref 25. h is obtained from the temperature variation of these γ values (see eq 3), assuming this variation to be linear. [d] Unmarked and starred V values are obtained from density data in ref 26 and 18, respectively. [e] The unbracketed and bracketed values are those obtained using V_0 and V respectively in eq 7 with $K_5 = \pi$. [f] Except where indicated, the ΔE_v(exptl) values are taken from ref 18, pp 435-439. Where the temperature is not shown explicitly in parentheses it is 298 K.

IV. Discussion

It is interesting to analyze the nature of the cavity radius r obtained from eq 5 that is necessary to predict ΔE_v in eq 7. As stated in the model adopted under section II, $2r$ in eq 5 is the distance of closest approach of spheres in a simple cubic arrangement. $2r$ is also equal to the hard-sphere diameter, σ, for nonpolar spherical molecules in the most compact packing arrangements, namely the fcc and hexagonal ones. This may be seen if one considers the interaction between two such nearest molecules a distance d_0 apart to be represented by an effective Lennard-Jones (12-6) potential, which incorporates many-body effects. $d_0 = 2^{1/6}(V/N)^{1/3}$ will then correspond to the location of the minimum in such a curve, and σ (corresponding to the point of zero potential) will be $\sigma = 2^{-1/6}d_0 = (V/N)^{1/3} = 2r$.[12]

Use of V_0 in eq 5 yields the low-temperature σ, σ_0, for spherical nonpolar molecules. For nonspherical molecules that generate an approximate sphere upon rotational averaging, it yields an average σ_0 if one assumes these hypothetical spheres to close pack at temperatures approaching 0 K. Columns two and three of Table II show the σ_0 and σ values obtained by using V_0 and V, respectively, in eq 5. Column four gives the σ values listed by Hirschfelder, Curtiss, and Bird[12] (where more than one value is reported, the value(s) closest to those in the previous two columns is (are) quoted). The last column gives the σ values obtained by Wilhelm and Battino[7] at 25 °C from gas solubility data for some of the liquids considered here using the scaled particle theory.[13] The σ_0 values of column two are smaller in magnitude than those of columns four and five in most cases. They are in much better agreement for the cryogenic liquids although they have not been corrected for zero-point energy contributions or many-body effects. Inclusion of the former effect would decrease the resultant σ_0 while consideration of the latter would increase it.[12]

The present σ values of column three are quite close to those in the next two columns. Equation 5 can thus provide another route for obtaining good estimates of σ in the case of liquids whose gas solubility data are lacking and for which such estimates are unavailable. This close agreement also supports a close packed local structure model rather than a simple cubic one for the liquids considered here at room temperature.

It is thus concluded that for spherical nonpolar molecules or for molecules that generate an approximate sphere upon rotational averaging, the radius of the cavity that needs to be created in the liquid when a molecule is transferred to the vapor phase is the hard-sphere molecular radius at a temperature approaching 0 K. For molecules that generate an ellipsoid of revolution varying to a large extent from a sphere, it is the "effective hard sphere" radius of the molecule in the liquid state. The liquid continuum favors the creation of as small a cavity within it as possible.

The present treatment is based on the premise that macroscopic surface tension γ values can be used for cavities of microscopic dimensions. This leads to a quantitative physical model that does not require an additional reduction in γ. Thermodynamic and statistical mechanical treatments have predicted such a reduction to exist as one goes to microscopic size cavities.[14-17] The work presented here does not exclude the need to consider such reduced γ values for cavities smaller

Table II. Comparison of Hard-Sphere Diameters (σ, Å) from (5) with Literature Values

Liquid	Eq 5 (using V_0)	Eq 5 (using V)	Ref 12	Ref 7
CCl_4	5.04	5.43	5.88	5.37
n-C_5H_{12}	5.14	5.76	5.77	
n-C_6H_{14}	5.46	6.01	5.92	5.92
Ethyl ether	5.06	5.57	5.54	
C_6H_6	4.88	5.28	5.27	5.26
Cyclohexane	5.14	5.64	6.09	5.63
CS_2	4.14	4.64	4.44	
SO_2	3.81	4.18	4.03, 4.29	
Br_2	4.00	4.39	4.27	
Cl_2	3.82	4.24	4.12	
$SiCl_4$	5.17	5.76		
CH_4	3.70	3.98	3.70, 3.82	
Xe	3.86	4.15	3.96, 4.10	
Kr	3.56	3.84	3.59, 3.68	
A	3.35	3.60	3.40, 3.47	
Ne	2.81	3.05	2.86	
O_2	3.26	3.60	3.43, 3.58	
N_2	3.57	3.87	3.68, 3.85	
NH_3	3.20	3.59		
Toluene	5.37	5.61	5.93	5.64
$CHCl_3$	4.70	5.11	5.43	
CH_3Cl	3.97	4.50	4.15	
n-C_8H_{18}	6.05	6.46	7.41	6.54
Dioxane		5.21		
Methylcyclohexane		5.96		5.99
m-Xylene	5.55	5.89		5.97
C_6H_5Cl	5.34	5.53		5.61
Nitrobenzene	5.30	5.55		5.74

than the hard-sphere radii of the molecules. It is also possible to consider the cavity radius to be larger than the hard-sphere one by a certain factor and then introduce a corresponding reduction in γ. For example, if the cavity radius was that corresponding to the minimum in Lennard-Jones (12-6) potential, one would need to introduce a microscopic $\gamma \approx 0.8\gamma_{mac}$. The current investigation only presents an internally self-consistent physical model with a predictive power within the limitations of the given assumptions.

The consistent positive deviation of the calculated ΔE_v values from the experimental ones for the cryogenic liquids (Table I) may be attributed to the need to use such a 13-26% reduced γ. Another explanation may be proposed for this deviation following the analysis of Harasima.[2] If the molecules in the liquid are assumed to execute harmonic oscillations, the mean potential energy of the motion and the mean kinetic energy are each equal to $(\frac{3}{2})kT$ per molecule. Since the former is lost on going to the vapor but is nearly unaffected on forming a surface, eq 1 reduces to $e_v \approx e_c^l - 3kT/2$ (neglecting e_i^v), or $\Delta E_v(\text{calcd}) - \Delta E_v(\text{exptl}) \approx 3RT/2$. The differences on the lhs of this equation as obtained from Table I are indeed quite close to $3RT/2$.

The present approach can account for the somewhat surprising empirical linear relation between $\gamma V^{2/3}$ (a free energy term) and ΔE_v (an energy term) first found by Hildebrand and Scott[18] and recently confirmed and extended for many liquids and liquid metals.[19,20] For the nonpolar spherical molecules of interest here, eq 7 becomes

$$\Delta E_v = \pi(2.0184 \times 10^{-3} V_0^{2/3} h) \qquad (7a)$$

$$= \{\pi(V_0/V)^{2/3}(h/\gamma)\}(2.0184 \times 10^{-3} V^{2/3}\gamma) \qquad (7b)$$

In order for the above mentioned linear relation to hold, the term in braces in eq 7b, referred to here as C, must remain relatively constant from one solvent to the next. Table I shows the approximate constancy of both the $(V_0/V)^{2/3}$ and (h/γ) factors. The thus calculated (and empirically found) C values for CCl_4, n-pentane, ethyl ether, benzene, cyclohexane, CS_2, SO_2, and Br_2, which lie very close to the K_5 line in Figure 1, are: 6.25 (6.31), 7.55 (7.54), 7.64 (7.58), 6.49 (6.41), 6.28 (6.40), 5.94 (6.07), 7.31 (7.45), and 5.86 (5.86). ΔE_v is seen to have a much better linear relation to $(hV_0^{2/3})$ than to $(\gamma V^{2/3})$.

For nonpolar spherical molecules giving a good fit to the K_5 line of Figure 1, eq 6 becomes

$$e_v/(V_0/N)^{2/3}h = \pi \qquad (6a)$$

This equation is the present counterpart of the equation introduced by Stefan in 1896[2,3] and alluded to in the Introduction, namely

$$q/(V/N)^{2/3}h = 2$$

$$q \equiv \Delta H_v/N$$

Harasima's modification[2] to Stefan's equation replaces q with $(q + kT/2)$ to take account of the potential energy of vibration of the molecules in the liquid state as discussed before.

The temperature dependence of ΔE_v in eq 7a is given by:

$$\left(\frac{\partial \Delta E_v}{\partial T}\right)_P = (2.0184 \times 10^{-3}\pi) V_0^{2/3} \times \left[\tfrac{2}{3}h\, V_0^{-1}\left(\frac{\partial V_0}{\partial T}\right)_P - T\left(\frac{\partial^2 \gamma}{\partial T^2}\right)_P\right] \qquad (8)$$

As $V_0^{-1}(\partial V_0/\partial T)_P$ is equal to three times the linear coefficient of expansion of the low-temperature hard-sphere diameter, $l_l \equiv \sigma_0^{-1}\cdot(\partial\sigma_0/\partial T)_P$, eq 8 provides a means of estimating this quantity from experimental determinations of the other two variables. Since $\Delta E_v \simeq \Delta H_v - RT$,[18] $(\partial\Delta E_v/\partial T)_P$ may be approximated from the $(\partial\Delta H_v/\partial T)_P$ estimated from heat-capacity measurements of vapor and liquid.[21] The variation of γ with temperature is very close to linear and $(\partial^2\gamma/\partial T^2)_P$ is extremely small. For CCl_4 and benzene it is $\sim 1.1 \times 10^{-3}$ ergs/(cm^2 °K^2).[22] The term arising from this on the rhs of eq 8 is 20-25% of the negative $(\partial\Delta E_v/\partial T)_P$ term at 25 °C as obtained from Wilhelm and Battino's $(\partial\Delta H_v/\partial T)_P$ values.[21] The resulting l_l estimates for these two liquids at room temperature are $(-0.69$ and $-0.76) \times 10^{-3}$ K^{-1}. The negative sign for l_l, and hence for $(\partial\sigma_0/\partial T)_P$, is in accordance with previous findings.[23] These magnitudes also compare favorably with the corresponding ones of $(-0.77$ and $-0.74) \times 10^{-3}$ K^{-1} obtained from Mayor's results[24] using the scaled particle theory.[13] Although one may use V instead of V_0 in eq 5-7 to obtain reasonably averaged hard-sphere diameters for nonspherical-type molecules, its use per se in these equations results in a positive $(\partial\Delta E_v/\partial T)_P$ since $(\partial V/\partial T)_P$ is positive for the liquids of interest here, a result contrary to experimental findings.

Equation 7a may also be used to obtain low-temperature molar volumes, and hence densities, from measured ΔE_v and h values.

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Approximate Selection Rules for Resonance Raman Spectroscopy[1]

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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