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Overtone resonance Raman scattering beyond the Condon approximation: Transform theory and vibronic properties

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The time correlator formalism is used to develop the expression for n th order (overtone) resonance Raman scattering (RRS) to include both Raman frequency shifts upon electronic excitation as well as non-Condon vibronic coupling. In particular the compact operator formalism recently introduced by Hizhnyakov and Tehver [*J. Raman Spectrosc.* **19**, 383 (1988)] to obtain several RRS correlators (including overtone scattering with frequency shift, but in the Condon approximation) is used to extend the theory. At the same time a formal advantage is achieved by the limited introduction of the Born–Oppenheimer approximation. Also transform relationships including non-Condon effects are given that link the Raman excitation profile of n th order scattering to the absorption spectrum. Finally, it is emphasized how all three vibronic parameters—potential energy surface displacement, Raman mode frequency changes, and the linear non-Condon coupling parameter—can be quantitatively determined without the need for absolute Raman cross-section measurements. The relative scattering intensity of the fundamental and three (or more) overtones suffices to fix the three. By way of application, the vibronic parameters are determined from published single wavelength overtone RRS in six molecules.

I. INTRODUCTION

Transform methods in resonance Raman scattering (RRS) are able to link the observed Raman excitation profile (REP) for a given scattered mode to the resonant absorption band (ABS). The method has been explored at various levels of approximation by several groups and has recently been reviewed by Page.¹ In its simplest form, one only requires a relative displacement of the minima of two identical harmonic oscillator functions to produce a meaningful REP from an electronically allowed transition. Beyond that, force constant changes between the two potential energy surfaces are introduced,^{2,3} mode mixing (Duschinsky rotation) is considered,^{2,4–6} vibronic effects in the transition moment are analyzed (non-Condon corrections),^{7–9} the adiabatic approximation is partly relaxed^{8,10,11} and an effort is made at proper temperature averaging. REP's of higher order scattering (overtones) as well as that of the fundamental can be examined. Recently, Hizhnyakov and Tehver (HT)¹² have presented an operator algebra approach to all of these approximations and been able to summarize the results in a highly compact form.

Given an observed REP for a given mode, it is even possible to achieve the inverse transform^{10,13} which, in principle, can produce the correct ABS that is responsible for the scattering—a particularly useful technique when ABS is buried among other nonactive absorption bands. In fact the practical aspect of RRS in general and transform methods in particular is their ability to determine properties of the reso-

nantly coupled potential energy surfaces, 1 (lower) and 2 (upper). However, usually absolute RRS measurements are needed to complete the task. The typical set of parameters are the fundamental frequencies ω_1 (given by the observed frequency of the scattered mode), ω_2 (not easily identified in a poorly resolved ABS), the bond length change Δ , and at least the linear non-Condon coupling parameter, m .

In the present study $\{\omega_2, \Delta, \text{ and } m\}$ are determined for several molecular species which exhibit strong overtone scattering in a mode that is easily identified. Since the same parameters $\{\omega_2, \Delta, \text{ and } m\}$ drive the overtone scattering, the problem soon becomes overdetermined and one is relieved of the need to make the difficult absolute RRS measurements.

To prepare for applications to overtone scattering we take the opportunity to review the theory and then explicitly incorporate the HT operator methods into the “limited adiabatic approach” to RRS presented in the literature.^{8,10} The latter points to a generality in which one needs to introduce the Born–Oppenheimer approximation only in the coordinate of the scattered mode, the remaining $3N-7$ space being left in the molecular eigenstate form. With the help of the work of HT, we present the expression for the REP for n th order scattering [$(n-1)$ th overtone], including the case of $\omega_1 \neq \omega_2$ and linear non-Condon effects. Duschinsky rotation involving the scattered mode is excluded and the mode considered is assumed to be not thermalized ($\hbar\omega_1 \gg kT$). The theory is applied to several molecules for which these approximations seem to be well suited and values for $\{\omega_2, \Delta, \text{ and } m\}$ are determined without resort to absolute RRS measurements.

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II. THEORY

A. The resonance Raman correlator in the limited adiabatic approximation

Let a sample of randomly oriented molecules undergo Raman scattering from an initial molecular eigenstate, i , into a final molecular eigenstate, f . If the incident laser frequency is ω_L and all the light scattered in all polarizations over 4π steradians at $\omega_L - \omega_f$ (integrated over the linewidth) is measured, the cross section per molecule is given as¹⁴

$$\sigma_R^f(\omega_L) = \frac{8\pi(\omega_L - \omega_f)^4}{9c^4\hbar^2} \sum_{\rho,\sigma} |\alpha_{\rho\sigma}(\omega_L)|_{fi}^2 \quad (1)$$

in which $[\alpha_{\rho\sigma}(\omega_L)]_{fi}$ is just the f, i th matrix element of the molecule-based $\rho\sigma$ th Cartesian tensor element of the (complex) molecular linear electrical susceptibility (the "molecular polarizability"). The circular Bohr frequency for the f, i th energy gap is $\omega_{fi} = (\Delta E_{fi}/\hbar)$. The frequency domain expression for $[\alpha_{\rho\sigma}(\omega_L)]_{fi}$ is just a field-free fragment of the second-order density operator, which has evolved under the incident laser field, the black-body field, and the molecular Hamiltonian

$$[\alpha_{\rho\sigma}(\omega_L)]_{fi} = \sum_e \left(\frac{\langle f|\rho|e\rangle\langle e|\sigma|i\rangle}{\omega_{ei} - \omega_L - i\gamma_{ei}} + \frac{\langle f|\sigma|e\rangle\langle e|\rho|i\rangle}{\omega_{ef} + \omega_L + i\gamma_{ie}} \right), \quad (2)$$

where the sum is over all molecular eigenstates and γ_{ei} represents the damping factor, or dephasing rate constant, for an e, i coherence (ρ and σ are molecule-based Cartesian components of the all-particle electric dipole operator).

When near or in resonance with an electronic transition, the principal contribution to $[\alpha_{\rho\sigma}(\omega_L)]_{fi}$ will be from the resonance that arises in the first term of Eq. (2). To arrive at general transform expressions for the resonant scattering of fundamentals and overtones, including non-Condon effects, by the simple operator algebra technique set forth by HT,¹² the terms of Eq. (2) that are near resonant are placed in the time domain by writing the complex denominator through its half-Fourier transform

$$[\alpha_{\rho\sigma}(\omega_L)]_{fi} = i \int_0^\infty d\tau e^{i\tau\omega_L} \sum_e e^{-i\tau(\omega_{ei} - i\gamma_{ei})} \langle f|\rho|e\rangle \times \langle e|\sigma|i\rangle. \quad (3)$$

The sum on e in Eq. (3) can be conveniently closed provided that the damping parameter, γ_{ei} , is algebraically separable [$\gamma_{ei} = (\gamma_e + \gamma_i)$], as already is the frequency difference [$\omega_{ei} \equiv (\omega_e - \omega_i)$]. To achieve formally such separation we introduce a non-Hermitian Hamiltonian, H , which consists of the full (Hermitian) molecular Hamiltonian, H , and a (anti-Hermitian) damping operator, D , such that (in circular frequency)

$$H|e\rangle = \omega_e|e\rangle, \quad D|e\rangle = i\gamma_e|e\rangle; \quad \text{or} \quad H|e\rangle = (\omega_e + i\gamma_e)|e\rangle. \quad (4a)$$

Introducing H defined in this way into Eq. (3) and closing on the complete molecular eigenstate basis set $\{|e\rangle\}$, we then have simply

$$[\alpha_{\rho\sigma}(\omega_L)]_{fi} = i \int_0^\infty d\tau e^{i\tau\omega_L} \langle f|\rho e^{-i\tau H^\dagger} \sigma e^{i\tau H}|i\rangle. \quad (4b)$$

Equation (4b) can be recognized as the Fourier transform of the time correlator for the two photon $f \leftarrow i$ transition, $[A_{\rho\sigma}]_{fi}$

$$[\alpha_{\rho\sigma}(\omega_L)]_{fi} = \int_{-\infty}^\infty d\tau e^{i\tau\omega_L} [A_{\rho\sigma}]_{fi} \quad (5a)$$

with the Raman correlator being given by (see also Ref. 12 for conjugate form)

$$[A_{\rho\sigma}]_{fi} = i\theta(\tau) \langle f|\rho e^{-i\tau H^\dagger} \sigma e^{i\tau H}|i\rangle, \quad (5b)$$

where $\theta(\tau)$ is the Heaviside step function.

It is of interest to note that the algebraic separation of the damping parameter, leading to Eq. (4a) and the success of closure, formally excludes "pure dephasing" (γ_{ei}) from the theory. By definition the pure dephasing rate constant is not separable into uncorrelated damping of states e and i . To include pure dephasing, density operator formalism is required. Once separability is introduced only state population decay can contribute to the damping. At this point there is neither explicit recognition of a resonance (though it is certainly called out by the kernel) nor is there any sign of the Born-Oppenheimer approximation needed to achieve an explicit transform relationship between an electronic absorption band (ABS) and the corresponding Raman excitation profile (REP) for every scattered vibration.

In a polyatomic molecule electronic absorption and Raman scattering are multimode in essence, often involving a significant part of the $3N-6$ space of nuclear motion. On the other hand, Raman scattering can focus on the scattering of a single mode at a time, the remaining $3N-7$ space participating in the REP much as it does in ABS. We can formally embrace this situation in its most general form by asking that the molecular Hamiltonian be parameterized only in the normal coordinate of the scattered vibration, otherwise all electronic coordinates and the remaining $3N-7$ nuclear coordinates serve as true variables. [However, to include mode-mixing (Dushinsky rotation) the B-O approximation limited to one coordinate must be relieved and extended to include the full sub-space of the mixing modes.] This limited adiabatic approach⁸ allows considerable generality in the $(3N-7)$ non-Raman space, including variable damping parameters as well as nonadiabatic effects to all orders. The usual potential energy hypersurfaces are formally absent, leaving only one-dimensional potential energy curves in the scattered coordinate. The molecular eigenenergies are parametric only in Q_a —the normal coordinate of the scattered mode—and are expanded in Q_a around equilibrium positions. Of course, the molecular eigenstates will cluster in groups $\{e'\}, \{g'\}$ to produce (normally) nearly harmonic potential curves $V_{e'}(Q_a)$ and $V_{g'}(Q_a)$ with well-defined equilibrium positions and second derivatives (force constants). This grouping corresponds to the conventional concept of a resonant and a ground electronic state each with well defined vibrational levels. In fact the present one-dimensional adiabatic approximation might best be thought of as the usual complete $[(3N-6)$ space] parameterization of the electronic Hamiltonian fol-

lowed by perturbative corrections to all orders in the $3N-7$ displacement coordinates of the eigenstates and eigenvalues. Coupling between the $3N-7$ space and that of the Raman coordinate is assiduously stricken to exclude, among other matters, Duschinsky rotation involving the Raman mode upon electronic excitation. For resonance Raman scattering, two potential energy curves are involved, called here, as in (HT), $V_2(Q_a)$ (upper) and $V_1(Q_a)$ (lower), with nuclear Hamiltonians H_2 and H_1 (both Hermitian). For harmonic potentials the latter, in number operator form, read simply

$$H_2 = T_2 + V_2 = \omega_2(\hat{a}_2^\dagger \hat{a}_2 + \frac{1}{2}), \quad (6a)$$

$$H_1 = T_1 + V_1 = \omega_1(\hat{a}_1^\dagger \hat{a}_1 + \frac{1}{2}) \quad (6b)$$

having eigenkets $\{|j_2\rangle\}$ and $\{|j_1\rangle\}$, respectively.

Furthermore, for the n th overtone transition of a given mode in the ground electronic state we write

$$|i\rangle \rightarrow |g'\rangle|j_1\rangle \equiv |g'\rangle|j\rangle, \quad (7a)$$

$$|f\rangle \rightarrow |g'\rangle|j_1+n_1\rangle \equiv |g'\rangle|j+n\rangle \quad (7b)$$

in which the subscripts 1 for the ground state are henceforth removed for simplicity. For the molecular eigenstate associated with resonances

$$|e\rangle \rightarrow |e'\rangle|j_2\rangle, \quad (7c)$$

where for Eqs. (7a) and (7b) we recognize the partitioning of the molecular Hamiltonian, H

$$H \rightarrow H_{g'} + H_1, \quad \text{with } H_{g'}|g'\rangle = \omega_{g'}|g'\rangle \quad (8a)$$

and for Eq. (7c) the partitioning of H

$$H \rightarrow H_{e'} + H_2, \quad \text{with } H_{e'}|e'\rangle = \omega_{e'}|e'\rangle \quad (8b)$$

in which $H_{g'}$ and $H_{e'}$ are not just the electronic Hamiltonians evaluated at ground and excited state equilibrium positions of the Raman active normal coordinate, but also include the full $3N-7$ nuclear coordinates of the non-Raman space without further approximation. The sum over molecular eigenstates also recognizes this factoring of state space with

$$\sum_e \rightarrow \sum_{e'} \sum_{j_2} \quad (9a)$$

in which the states $\{e'\}$ are those that carry transition dipole strength to (and from) the ground state in the resonant band. Furthermore, whenever the damping parameter appears, it, too, is partitioned into the two spaces

$$\gamma_{ei} \rightarrow \gamma_{e'i'} + \gamma_{j_2j_1} = \gamma_{e'i'} + \gamma \quad (9b)$$

in which $\gamma_{j_2j_1}$ represents the damping contribution from the Raman subspace only. It is conventionally (and conveniently) taken to be a constant, γ , for all relevant $\{j_2j_1\}$. For many applications at ordinary temperature j_1 is often an entirely unexcited Raman mode whose $\gamma_{j_1} = 0$. In that case $\gamma_{j_2} = \gamma$ and its assumed constancy claims that the decay parameter of the Raman mode in the excited electronic state does not change with its degree of excitation. However, the $\gamma_{e'i'}$ contribution to the damping can vary with the energy of excitation in an unconstrained manner. Li and Champion

have explored a model that relieves the constant γ assumption as applied to transform theory.¹⁵ Finally,

$$\sigma_R^{fi} \rightarrow \sigma_R^{(j+n)j}. \quad (9c)$$

With this limited adiabatic point of view and related statements Eqs. (7)–(9) one can return to Eq. (3), introduce Eqs. (6)–(9) and close the sum on j_2 , but not on e' . At this point one obtains

$$\begin{aligned} & [\alpha_{\rho\sigma}(\omega_L)]_{g'(j+n),g'j} \\ &= i \int_0^\infty d\tau e^{i\tau\omega_L} e^{-\tau\gamma} \left(\sum_{e'} e^{-i\tau(\omega_{e'g'} - i\gamma_{e'g'})} \right. \\ & \quad \left. \times \langle j+n | (g'|\rho|e') e^{-i\tau H_2} (e'|\sigma|g') e^{i\tau H_1} |j \rangle \right). \end{aligned} \quad (10)$$

Writing the Cartesian components of the electric transition moments in the non-Raman space as $(M_\rho)_{e'g'}$, $(M_\sigma)_{e'g'}$, the Raman correlator in this limited adiabatic approximation becomes [see Eq. (5b)]

$$\begin{aligned} [A_{\rho\sigma}(\tau)]_{j+n,j} &= i\theta(\tau) e^{-\tau\gamma} \sum_{e'} e^{-i\tau(\omega_{e'g'} - i\gamma_{e'g'})} \\ & \quad \times \langle j+n | (M_\rho)_{g'e'} e^{-i\tau H_2} (M_\sigma)_{e'g'} e^{i\tau H_1} |j \rangle. \end{aligned} \quad (11)$$

This expression is close to that given by HT except that we have recognized in a quite unrestricted way the role of the non-Raman space. At this point we note that throughout this work the development is consistently the (negative) conjugate to that presented by HT. [Equivalently, were the phase of the HT representation of correlators and polarizabilities ϕ , then ours is $(\pi - \phi)$.] Thus our Eqs. (2) and (3) are exactly the negative and the conjugate of HT's Eqs. (1) and (2), respectively. This has the sole purpose of having the present development be based on the more conventional expression for the Raman polarizability [Eq. (2)]. Finally, Eq. (10) becomes

$$[\alpha_{\rho\sigma}(\omega_L)]_{j+n,j} = \int_{-\infty}^\infty d\tau e^{i\tau\omega_L} [A_{\rho\sigma}(\tau)]_{j+n,j}. \quad (12)$$

At the same time the general expression for the linear absorption cross section, $\sigma_A^{ii}(\omega_L)$, from the i th molecular level into all reasonably excited states in an isotropic medium is

$$\sigma_A^{ii}(\omega_L) = \frac{4\pi\omega_L}{3c} \sum_\rho \text{Im}[\alpha_{\rho\rho}(\omega_L)]_{i,i} \quad (13)$$

or, in the above limited adiabatic approximation, with absorption from level $|g\rangle|j\rangle$, we have

$$\sigma_A^{jj}(\omega_L) = \frac{4\pi\omega_L}{3c} \sum_\rho \text{Im}[\alpha_{\rho\rho}(\omega_L)]_{j,j}, \quad (14)$$

where [Eq. (5a)]

$$[\alpha_{\rho\rho}(\omega_L)]_{j,j} = \int_{-\infty}^\infty d\tau e^{i\tau\omega_L} [A_{\rho\rho}(\tau)]_{j,j} \quad (15)$$

and with Eq. (11)

$$[A_{\rho\rho}(\tau)]_{j,j} = i\theta(\tau)e^{-\gamma\tau} \sum_{e'} e^{-i\tau(\omega_{e',g'} - i\gamma_{e',g'})} \\ \times \langle j|(M_{\rho})_{g',e'} e^{-i\tau H_2}(M_{\rho})_{e',g'} e^{i\tau H_1}|j\rangle. \quad (16)$$

This is just the diagonal matrix element of the $\rho\rho$ th Cartesian tensor component of the vibronic absorption correlator. The fundamental task of transform theory is to link the $\rho\rho$ th Cartesian tensor component of the diagonal $[(j,j)]$ vibronic absorption correlator [Eq. (16)] to the off-diagonal version $[(j+n,j)]$ [Eq. (11)]. Recognizing that the ladder operators of two different harmonic oscillators are linearly related, Hizhnyakov and Tehver have presented a particularly succinct algebra for accomplishing this task. Before proceeding we briefly discuss the intrusion of ensemble effects into the problem.

B. Ensemble effects (Ref. 8)

In the laboratory, an observed (linear) absorption cross section, $\text{ABS}(\omega)$ represents an ensemble averaged cross section over all initial states recognizing both the thermal distribution of molecules over initial states as well as a possible site distribution, or inhomogeneity of vibronic Bohr frequencies (energy gaps). Thus for $\Omega_{g',j}$ representing the weighting (thermal and otherwise) of the initial state $\{|g'\rangle|j\rangle\}$ we must write

$$\text{ABS}(\omega) = \frac{3c}{4\pi} \sum_{g',j} \Omega_{g',j} \sigma_A^{jj}(\omega) \quad (17)$$

and similarly for the observed resonance Raman spectrum or Raman excitation profile $[\text{REP}(\omega)]$

$$\text{REP}(\omega) = \sum_{g',j} \Omega_{g',j} \sigma_R^{j(j+n)}(\omega). \quad (18)$$

(In both cases the g' label on the cross sections is suppressed for convenience.)

Now as Eq. (14) [via Eqs. (15) and (16)] is linear in the correlator while Eq. (1) [via Eq. (12)] is quadratic in the correlator, Eqs. (17) and (18) represent ensemble averaging of the correlator on the linear and quadratic level, respectively. The link between ABS and REP is formally ensemble (and temperature) dependent. This is a problem in principle and has been addressed by several workers⁸ where sample cases were explored. In fact theoretical work^{16,17} finds conditions for which the amplitude level temperature averaging in ABS achieves an approximate temperature averaging for the REP. In the present study the often manageable but complicating issue of ensemble effects is neglected for the scattered mode. However, we point out that in the limited adiabatic treatment used here amplitude level temperature averaging in the $3N-7$ space is implicitly present. We expect that for the systems treated—fundamental and overtone scattering from modes whose frequencies are in considerable excess of kT —such neglect is not a serious one.

C. The non-Condon n th order RRS correlator, $A_n^{\text{NC}}(\tau)$, in terms of the non-Condon absorption correlator, $A_0^{\text{NC}}(\tau)$, and transform relationships

The task now is to develop the link between the n th order Raman correlator and the absorption correlator in the presence of the non-Condon correction (at the linear level) to the transition moment. In Sec. I the n th order non-Condon (NC) Raman correlator is given in terms of the Condon (C) correlators with help from material in the Appendices. Recursion relationships among the Condon correlators obtained by HT are then introduced in Sec. II to express the NC Raman correlators in terms of the Condon absorption correlator. The NC absorption correlator is likewise given in terms of the Condon absorption correlator so that the latter can be eliminated to achieve our objective. In Sec. III the corresponding transform laws that link n th order Raman excitation profiles to the absorption profile are developed, including non-Condon effects.

1. The non-Condon correlator in terms of the Condon correlator

We return to Eq. (11) for the n th order Raman correlator, restrict our consideration to resonance with a uniquely polarized transition ($\rho=\sigma$), and consider an explicit, simple, dependence of the molecular transition moment $(M_{\rho})_{g',e'}$ on the coordinate of the Raman active vibration. Thus we write for a linear non-Condon (NC) coupling in the Raman active mode

$$(M_{\rho})_{g',e'} = (M_{\rho})_{g',e'}^{(0)} [1 + m(\hat{a}_1 + \hat{a}_1^{\dagger})] \quad (19)$$

in which m represents a dimensionless average linear NC coupling of the transition moment to the Raman active mode (whose ground state harmonic potential is characterized by the raising and lowering operators \hat{a}_1^{\dagger} and \hat{a}_1). This non-Condon coupling parameter, m , can be read as the fractional change of the transition moment caused by one rms displacement along the Raman mode coordinate in the ground state. $(M_{\rho})_{g',e'}^{(0)}$ continues to contain implicitly all of the nuclear coordinates of the $3N-7$ non-Raman space including their unconstrained Condon and non-Condon role (see Refs. 11 and 8). It is only the Raman active coordinate that has been treated explicitly at the linear non-Condon level.

Some necessary limitations to the present limited adiabatic model have crept in. First, in considering a specific molecule-based Cartesian transition moment (ρ), we have excluded the possibility of a rotating moment with (e',g') . Second, to maintain the separability of the Raman space from the non-Raman space we have been obliged to keep the dimensionless NC coupling constant, m , independent of (e',g') . It is therefore declared to be an “average” NC coupling parameter. These constraints are standard ones in the usual full B–O approach to the problem.

First we simplify our notation

$$\hat{M} \equiv [1 + m(\hat{a}_1 + \hat{a}_1^{\dagger})], \quad \hat{B} \equiv e^{-i\tau H_2}, \quad \hat{C} \equiv e^{i\tau H_1}. \quad (20)$$

We can write now

$$\begin{aligned} & \langle j+n | (M_\rho)_{g'e'} e^{-i\tau H_2} (M_\rho)_{e'g'} e^{i\tau H_1} | j \rangle \\ &= | [M_\rho^{(0)}]_{g'e'} |^2 \langle j+n | \hat{M} \hat{B} \hat{M} \hat{C} | j \rangle \end{aligned} \quad (21)$$

and then the n th order resonance Raman correlator [Eq. (11)] becomes

$$\begin{aligned} A_n^{\text{NC}}(\tau) &= i\theta(\tau) e^{-\gamma\tau} \sum_{e'} e^{-i\tau(\omega_{e'g'} - i\gamma_{e'g'})} | [M_\rho^{(0)}]_{g'e'} |^2 \\ &\times \langle j+n | \hat{M} \hat{B} \hat{M} \hat{C} | j \rangle \end{aligned} \quad (22)$$

in which we have written $[A_{\rho\rho}(\tau)]_{j,j+n} \equiv A_n^{\text{NC}}(\tau)$ in this linear NC approximation.

Now given that $\langle n | = \langle 0 | (\hat{a}_1)^\dagger (n!)^{-1/2}$, we write for convenience $(\hat{a}_1)^\dagger \equiv \hat{A}_n(1)$. Then we take $j=0$ to dominate the correlator for the j part of the thermal average in Eq. (17) ($\hbar\omega_1 \gg kT$). Thus

$$\begin{aligned} A_n^{\text{NC}}(\tau) &\approx i\theta(\tau) (n!)^{-1/2} e^{-\gamma\tau} \sum_{e'} e^{-i\tau(\omega_{e'g'} - i\gamma_{e'g'})} \\ &\times | [M_\rho^{(0)}]_{g'e'} |^2 \langle 0 | \hat{A}_n(1) \hat{M} \hat{B} \hat{M} \hat{C} | 0 \rangle \end{aligned} \quad (23)$$

and for the absorption correlator ($n=0$)

$$\begin{aligned} A_0^{\text{NC}}(\tau) &\approx i\theta(\tau) e^{-\gamma\tau} \sum_{e'} e^{-i\tau(\omega_{e'g'} - i\gamma_{e'g'})} \\ &\times | [M_\rho^{(0)}]_{g'e'} |^2 \langle 0 | \hat{M} \hat{B} \hat{M} \hat{C} | 0 \rangle. \end{aligned} \quad (24)$$

We note that the approximate thermal averaging achieved at the correlator level (see Refs. 1 and 12) remains in effect here as well, as far as the $3N-7$ non-Raman space (the averaging over g') is concerned. It is only the Raman space (the j space) that has been truncated to the unexcited level.

In Appendix A [Eq. (A8)] we show that to a good approximation the n th order NC Raman correlator can be related to A_n^C , A_{n+1}^C and A_{n-1}^C , the n th, $(n+1)$ th and $(n-1)$ th order Condon Raman correlators [$m=0$, $\hat{M}=1$ in Eq. (23)] as follows:

$$\begin{aligned} A_n^{\text{NC}}(\tau) &= \left[1 + \frac{mp}{q+r} (e^{i\tau\omega_2} + e^{-i\tau\omega_2} - 2) \right] A_n^C(\tau) + m(n \\ &+ 1)^{1/2} \left(1 + \frac{q}{q+r} e^{i\tau\omega_2} + \frac{r}{q+r} e^{-i\tau\omega_2} \right) A_{n+1}^C(\tau) \\ &+ mn^{1/2} \left(1 + \frac{q}{q+r} e^{i\tau\omega_2} + \frac{r}{q+r} e^{-i\tau\omega_2} \right) A_{n-1}^C(\tau). \end{aligned} \quad (25)$$

The absorption correlator is obtained using $n=0$ in Eq. (25)

$$\begin{aligned} A_0^{\text{NC}}(\tau) &= \left[1 + \frac{mp}{q+r} (e^{i\tau\omega_2} + e^{-i\tau\omega_2} - 2) \right] A_0^C(\tau) \\ &+ m \left(1 + \frac{q}{q+r} e^{i\tau\omega_2} + \frac{r}{q+r} e^{-i\tau\omega_2} \right) A_1^C(\tau). \end{aligned} \quad (26)$$

As shown in Appendix C the parameters p , q , and r in these equations are given by

$$\begin{aligned} p &= (-\Delta) \left(\frac{\pi c}{\hbar} \right)^{1/2} (\mu)^{1/2} (\tilde{\nu}_2)^{1/2}, \\ q &= \frac{(\tilde{\nu}_2 + \tilde{\nu}_1)}{2(\tilde{\nu}_2 \tilde{\nu}_1)^{1/2}}, \\ r &= \frac{(\tilde{\nu}_2 - \tilde{\nu}_1)}{2(\tilde{\nu}_2 \tilde{\nu}_1)^{1/2}} \end{aligned} \quad (27)$$

in which Δ is the displacement of the equilibrium position of the excited-state potential energy curve (it is one dimensional), $R_e(2)$, from that $R_e(1)$ of the ground state curve along the Raman mode coordinate [$\Delta = R_e(2) - R_e(1)$], μ is the reduced mass of the Raman oscillator, and $\tilde{\nu}_2$ and $\tilde{\nu}_1$ are the Raman mode wavenumbers in the excited and ground states, respectively (in cm^{-1} , with $\omega = 2\pi c \tilde{\nu}$).

Equations (25) and (26) establish the desired relationship between non-Condon and Condon correlators for n th order RRS. We are now ready to introduce the recursion relationships among the Condon Raman correlators developed by HT and finally to link the non-Condon Raman correlators at any order to the non-Condon absorption correlator.

2. Introduction of the HT recursion formulas for the Condon correlators to obtain $A_n^{\text{NC}}(\tau)$ in terms of $A_0^{\text{NC}}(\tau)$

HT have given recursion formulae for the Condon correlators for the unexcited state. These are derived from the $(\alpha_{\rho\sigma})_{if}$ polarizability component. For our choice of phase, the $(\alpha_{\rho\sigma})_{fi}$ matrix element is used here instead. Hence it is the complex conjugates of the HT correlators which are required. From this we obtain for n even ($n=2k$)

$$A_{2k}^C(\tau) = [(2k)!]^{1/2} \sum_{s=0}^k \frac{\xi^{2s} \zeta^{k-s}}{(k-s)! 2^{k-s} (2s)!} A_0^C(\tau) \quad (28a)$$

and for n odd [$n=(2k+1)$]

$$\begin{aligned} A_{2k+1}^C(\tau) &= [(2k+1)!]^{1/2} \\ &\times \sum_{s=0}^k \frac{\xi^{2s+1} \zeta^{k-s}}{(k-s)! 2^{k-s} (2s+1)!} A_0^C(\tau) \end{aligned} \quad (28b)$$

in which we have put $m=0$ in Eq. (23) and defined for our limited B-O approach. Because the present treatment is consistently (negative) conjugate to that of HT, the parameters in Eqs. (28) must be the conjugates of those found in the HT treatment. Thus here we write

$$\xi = \bar{\xi} \frac{e^{-i\tau\omega_2} - 1}{1 - \delta e^{-i\tau\omega_2}} \quad \text{and} \quad \zeta = \delta \frac{e^{-2i\tau\omega_2} - 1}{1 - \delta^2 e^{-2i\tau\omega_2}}, \quad (29a)$$

$$\bar{\xi} \equiv \frac{p}{q} \quad \text{and} \quad \delta \equiv \frac{r}{q}. \quad (29b)$$

The parameters $\{p, q, r\}$ are given in Eqs. (27). The two remaining HT parameters, $\bar{\xi}$ and δ in Eqs. (29) are then

$$\bar{\xi} = \frac{p}{q} = - \left(\frac{8\pi^2 c}{h} \right)^{1/2} (\mu \tilde{\nu}_1)^{1/2} \Delta \frac{\tilde{\nu}_2}{\tilde{\nu}_1 + \tilde{\nu}_2} \approx -2.43557 \times 10^{-3} (\mu \tilde{\nu}_1)^{1/2} \Delta \frac{\tilde{\nu}_2}{\tilde{\nu}_1 + \tilde{\nu}_2} \quad (30a)$$

with

$$[\mu] = 1 \text{ amu}, \quad [\tilde{\nu}] = 1 \text{ cm}^{-1}, \quad [\Delta] = 1 \text{ pm}$$

and

$$\delta = \frac{r}{q} = \frac{\tilde{\nu}_2 - \tilde{\nu}_1}{\tilde{\nu}_2 + \tilde{\nu}_1}. \quad (30b)$$

Equation (26) can be greatly simplified. For $n=1$ ($k=0$) Eq. (28b) becomes

$$A_1^C(\tau) = \xi A_0^C(\tau). \quad (31a)$$

Using the approximations

$$\delta^2 \ll 1, \quad \delta \ll 1 \Rightarrow \delta^2 e^{-2i\tau\omega_2} \ll 1, \quad m\delta \ll 1, \quad m^2 \ll 1 \quad (31b)$$

the non-Condon absorption correlator in terms of the Condon one [Eq. (26)] becomes

$$A_0^{\text{NC}}(\tau) = (1 + 2m\xi) A_0^C(\tau) \quad (31c)$$

or, to order $m\xi$

$$A_0^C(\tau) \approx (1 - 2m\xi) A_0^{\text{NC}}(\tau). \quad (31d)$$

We shall proceed to assemble the $A_n^{\text{NC}}(\tau) \leftrightarrow A_0^{\text{NC}}(\tau)$ relationship using Eqs. (25), (28), and (31d) under the assumptions (31b).

For a wide range of real cases the parameters ξ and ζ can be written then as

$$\xi \approx \bar{\xi} (e^{-i\tau\omega_2} - 1) (1 + \delta e^{-i\tau\omega_2}), \quad (32a)$$

$$\zeta \approx \delta (e^{-2i\tau\omega_2} - 1). \quad (32b)$$

Equation (25) becomes for $n=n_e$ (even)

$$A_{n_e}^{\text{NC}}(\tau) = \sum_{s=0}^{n_e/2} \left[\frac{n_e^{1/2}}{2s} C + \frac{[(n_e+1)n_e]^{1/2}}{(2s+1)2s} (n_e+1)^{1/2} C_+ + n_e^{1/2} C_- \right] (1-2m\xi) [(n_e-1)!]^{1/2} \times \frac{\xi^{2s-1} \zeta^{(n_e/2)-s}}{\left(\frac{n_e}{2}-s\right)! 2^{(n_e/2)-s} (2s-1)!} A_0^{\text{NC}}(\tau) \quad (33a)$$

and for $n=n_0$ (odd)

$$A_{n_0}^{\text{NC}}(\tau) = \sum_{s=0}^{(n_0-1)/2} \left[\frac{n_0^{1/2}}{2s+1} C + \frac{[(n_0+1)n_0]^{1/2}}{(2s+2)(2s+1)} (n_0+1)^{1/2} C_+ + n_0^{1/2} C_- \right] (1-2m\xi) [(n_0-1)!]^{1/2} \times \frac{\xi^{2s} \zeta^{(n_0-1)/2-s}}{\left(\frac{n_0-1}{2}-s\right)! 2^{(n_0-1)/2-s} (2s)!} A_0^{\text{NC}}(\tau), \quad (33b)$$

where C , C_+ , and C_- are given by

$$C = \xi \left[1 + \frac{m\bar{\xi}}{1+\delta} (e^{i\tau\omega_2} + e^{-i\tau\omega_2} - 2) \right], \quad (34a)$$

$$C_+ = \xi^2 m \left(1 + \frac{e^{i\tau\omega_2}}{1+\delta} + \frac{\delta e^{-i\tau\omega_2}}{1+\delta} \right), \quad (34b)$$

$$C_- = m \left(1 + \frac{e^{-i\tau\omega_2}}{1+\delta} + \frac{\delta e^{i\tau\omega_2}}{1+\delta} \right). \quad (34c)$$

After performing some algebraic calculations,¹⁸ within the approximations (31b) and introducing the notations $\hat{\beta} \equiv e^{-i\tau\omega_2}$, $k_e \equiv (n_e/2)$, $k_0 \equiv (n_0-1)/2$ Eqs. (33a) and (33b) become

$$A_{n_e}^{\text{NC}}(\tau) = (n_e!)^{1/2} \sum_{s=0}^{k_e} \frac{\xi^{2s-1} \zeta^{k_e-s}}{(k_e-s)! 2^{k_e-s} (2s)!} \bar{\xi} A_0^{\text{NC}}(\tau) \left\{ \left[\delta + 2 \frac{k_e-s}{2s+1} m\bar{\xi} \right] \hat{\beta}^2 + \left[1 - \delta + (2s) \frac{m}{\bar{\xi}} - 2 \frac{k_e-s}{2s+1} m\bar{\xi} \right] \hat{\beta} + \left[(2s) \frac{m}{\bar{\xi}} - 1 - 2 \frac{k_e-s}{2s+1} m\bar{\xi} \right] + \left[2 \frac{k_e-s}{2s+1} m\bar{\xi} \right] \hat{\beta}^{-1} \right\} \quad (35a)$$

and

$$A_{n_0}^{\text{NC}}(\tau) = (n_0!)^{1/2} \sum_{s=0}^{k_0} \frac{\xi^{2s} \zeta^{k_0-s}}{(k_0-s)! 2^{k_0-s} (2s+1)!} \bar{\xi} A_0^{\text{NC}}(\tau) \left\{ \left[\delta + 2 \frac{k_0-s}{2s+2} m\bar{\xi} \right] \hat{\beta}^2 + \left[1 - \delta + (2s+1) \frac{m}{\bar{\xi}} - 2 \frac{k_0-s}{2s+2} m\bar{\xi} \right] \hat{\beta} + \left[(2s+1) \frac{m}{\bar{\xi}} - 1 - 2 \frac{k_0-s}{2s+2} m\bar{\xi} \right] + \left[2 \frac{k_0-s}{2s+2} m\bar{\xi} \right] \hat{\beta}^{-1} \right\}. \quad (35b)$$

Using Eqs. (32) for ξ and ζ , expanding ξ^{2s} , and ζ^k , ($k=k_e, k_0$), approximating $(1+\delta\hat{\beta})^j$ as $1+j\delta\hat{\beta}$ and using the notation $x \equiv 2m\bar{\xi}$, $k_e \equiv (k_e-s)/(2s+1)$, $k_0 \equiv (k_0-s)/(2s+2)$ yields the final form of the relationship $A_n^{\text{NC}}(\tau) \leftrightarrow A_0^{\text{NC}}(\tau)$

$$A_{n_e}^{\text{NC}}(\tau) = (n_e!)^{1/2} \sum_{s=0}^{k_e} \frac{\xi^{2s} \delta^{k_e-s} (k_e+s-1)!}{2^{k_e-s} (2s)!} \sum_{t=0}^{k_e+s-1} \frac{(-1)^t}{t!(k_e+s-1-t)!} \sum_{u=0}^{k_e-s} \frac{1}{u!(k_e-s-u)!} \left\{ [(2s)\delta + k_e x] \hat{\beta}^{n_e-t-u+1} \right. \\ \left. + \left[1 - (2s) \left(\delta - \frac{m}{\xi} \right) - k_e x \right] \hat{\beta}^{n_e-t-u} + \left((2s) \frac{m}{\xi} - 1 - k_e x \right) \hat{\beta}^{n_e-t-u-1} + k_e x \hat{\beta}^{n_e-t-u-2} \right\} A_0^{\text{NC}}(\tau) \quad (36a)$$

and

$$A_{n_0}^{\text{NC}}(\tau) = (n_0!)^{1/2} \sum_{s=0}^{k_0} \frac{\xi^{2s+1} \delta^{k_0-s} (k_0+s)!}{2^{k_0-s} (2s+1)!} \sum_{t=0}^{k_0+s} \frac{(-1)^t}{t!(k_0+s-t)!} \sum_{u=0}^{k_0-s} \frac{1}{u!(k_0-s-u)!} \left\{ [(2s+1)\delta + k_0 x] \hat{\beta}^{n_0-t-u+1} \right. \\ \left. + \left[1 - (2s+1) \left(\delta - \frac{m}{\xi} \right) - k_0 x \right] \hat{\beta}^{n_0-t-u} + \left[(2s+1) \frac{m}{\xi} - 1 - k_0 x \right] \hat{\beta}^{n_0-t-u-1} + k_0 x \hat{\beta}^{n_0-t-u-2} \right\} A_0^{\text{NC}}(\tau). \quad (36b)$$

This is the desired link between the n th order Raman correlator and the absorption correlator at the non-Condon level (in its linear approximation). Next, the transform relationships for n th Raman excitation profiles are developed.

In transform applications the complex linear polarizability $[\alpha_0(\omega)]$ has often been called $\Phi(\omega)$. It relates to ABS through the Hilbert transform

$$\alpha_0^{\text{NC}}(\omega) \equiv \Phi(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\text{ABS}(\omega')}{\omega'^2 - \omega^2} d\omega' \\ + i \frac{\text{ABS}(\omega)}{\omega}. \quad (39)$$

3. The non-Condon transform relationships for overtone RRS

Now the Fourier transform [Eq. (12)] of the NC n th order Raman correlator [Eq. (25)] produces the n th order NC polarizability (ρ th tensor element) (with $\omega_L \equiv \omega$)

$$\alpha_n^{\text{NC}}(\omega) = \int_{-\infty}^\infty d\tau e^{i\tau\omega} A_n^{\text{NC}}(\tau) \quad (37)$$

of which at zeroth order ($n=0$) one has just the linear polarizability whose Im part leads to the absorption spectrum (ABS). Thus [see Eq. (14)]

$$\text{Im}[\alpha_0^{\text{NC}}(\omega)] = \frac{3c}{4\pi\omega} \sigma_A^{00}(\omega) \equiv \frac{\text{ABS}(\omega)}{\omega}. \quad (38)$$

The frequency displacement operator $\hat{\beta} \equiv e^{-i\omega_2\tau}$ appears in $A_n^{\text{NC}}(\tau)$ as various powers through Eqs. (35)–(36). This operator simply shifts the frequency of the Fourier kernel [as in Eq. (37)]. Thus

$$\int_{-\infty}^\infty d\tau e^{i\tau\omega} \hat{\beta}^s \dots = \int_{-\infty}^\infty d\tau e^{i\tau(\omega - s\omega_2)} \dots \quad (40)$$

and the Fourier transform of the Raman correlator [Eq. (37)] in the presence of a term containing $\hat{\beta}^s$, [see Eqs. (36)] will produce a Raman polarizability whose frequency argument has been *downshifted* by $s\omega_2$ from the incident laser frequency, ω .

The Fourier transform of Eqs. (36a,b) then gives for $n = n_e$ (even)

$$\alpha_{n_e}^{\text{NC}}(\omega) = (n_e!)^{1/2} \sum_{s=0}^{k_e} \frac{\xi^{2s} \delta^{k_e-s} (k_e+s-1)!}{2^{k_e-s} (2s)!} \sum_{t=0}^{k_e+s-1} \frac{(-1)^t}{t!(k_e+s-1-t)!} \sum_{u=0}^{k_e-s} \frac{1}{u!(k_e-s-u)!} \left\{ [(2s)\delta + k_e x] \Phi(1) \right. \\ \left. + \left[1 - (2s) \left(\delta - \frac{m}{\xi} \right) - k_e x \right] \Phi(0) + \left((2s) \frac{m}{\xi} - 1 - k_e x \right) \Phi(-1) + (k_e x) \Phi(-2) \right\},$$

$$\text{where } \Phi(j) \equiv \Phi[\omega - (n_e - t - u + j)\omega_2] \quad (41a)$$

and for $n = n_0$ (odd)

TABLE I. Raman data employed in the calculations. ${}^1T_2 \leftarrow {}^1A_1$ transition. Any Jahn–Teller and/or site splitting of the 1T_2 state is assumed to be negligible in the present theoretical/experimental treatment.

System	$\tilde{\nu}_{eg}^*$ (cm^{-1})	Excitation wavelength (nm)	Raman wave number (cm^{-1})	1st harmonic relative intensity	2nd harmonic relative intensity	3rd harmonic relative intensity	4th harmonic relative intensity
TiI_4^a	19400	514.5	161	1.0	0.47	0.24	0.11
$\text{KMnO}_4:\text{KClO}_4^b$	~ 19000	514.5	847	1.0	1.0	0.26	0.09
K_2MnO_4^c	~ 17000	568.2	814	1.0	0.18	0.06	0.01
$[\text{NBu}_4]_2[\text{WS}_4]^d$	24650	406.7	478	1.0	0.32	0.16	0.07
$[\text{NH}_4]_2[\text{WS}_4]^d$	~ 24200	406.7	488	1.0	0.36	0.23	0.12
$[\text{NBu}_4]_2[\text{MoS}_4]^e$	20230	476.5	451	1.0	0.85	0.64	0.36

^aReference 19.^dReference 22.^bReference 20.^eReference 23.^cReference 21.

$$\alpha_{n_0}^{\text{NC}}(\omega) = (n_0!)^{1/2} \sum_{s=0}^{k_0} \frac{\tilde{\xi}^{2s+1} \delta^{k_0-s}(k_0+s)!}{2^{k_0-s}(2s+1)!} \sum_{t=0}^{k_0+s} \frac{(-1)^t}{t!(k_0+s-t)!} \sum_{u=0}^{k_0-s} \frac{1}{u!(k_0-s-u)!} \left\{ [(2s+1)\delta + k_0 x] \Phi(1) \right. \\ \left. + \left[1 - (2s+1) \left(\delta - \frac{m}{\tilde{\xi}} \right) - k_0 x \right] \Phi(0) + \left((2s+1) \frac{m}{\tilde{\xi}} - 1 - k_0 x \right) \Phi(-1) + (k_0 x) \Phi(-2) \right\},$$

where $\Phi(j) \equiv \Phi[\omega - (n_0 - t - u + j)\omega_2]$. (41b)

The polarizability function, $\Phi(\omega)$, is available from the experimental ABS [Eq. (39)].

Finally, the n th order RR scattering cross section is obtained using Eqs. (41) in Eq. (1)

$$\text{REP}_n(\omega) = \text{const} |\alpha_n^{\text{NC}}(\omega)|^2. \quad (42)$$

The proportionality constant is essential only for absolute REP measurements.

III. APPLICATIONS AND THE DETERMINATION OF VIBRONIC PROPERTIES

In this section the theoretical results described earlier are tested by calculating $\tilde{\nu}_2$, Δ and m for a number of molecules. These results are then compared with previously published ones.

Equation (42) can be written for any single given excitation frequency ω and for $n=1$ to 4, obtaining a system of four simultaneous equations. The experiment-dependent proportionality constant can be eliminated immediately (provided one is careful, when necessary, to correct for the relative sensitivity of the apparatus over the spectral range of the Raman scattering from the fundamental to the highest overtone used in the data set. Data employed have been corrected already for the spectral response of the instrument.^{19–24}) Only *relative* measurements are needed^{25–28} and one can write

$$\frac{\text{REP}_i(\omega)}{\text{REP}_1(\omega)} = \frac{|\alpha_i^{\text{NC}}(\omega)|^2}{|\alpha_1^{\text{NC}}(\omega)|^2}, \quad i=2,3,4. \quad (43)$$

Solving this system of three nonlinear algebraic equations is equivalent¹⁸ to minimizing the function

$$F(\Delta, \omega_2, m) = \sum_{i=2}^4 \left[\left(\frac{|\alpha_i^{\text{NC}}(\omega, \Delta, \omega_2, m)|^2}{|\alpha_1^{\text{NC}}(\omega, \Delta, \omega_2, m)|^2} \right)_{\text{calculated}} - \left(\frac{\text{REP}_i(\omega)}{\text{REP}_1(\omega)} \right)_{\text{experimental}} \right]^2. \quad (44)$$

The function $F(\Delta, \omega_2, m)$ can have several minima as it is nonlinear in its component variables. Classical iterative methods for solving nonlinear equations²⁹ require a good starting approximate solution towards which the iteration will, eventually, converge. This approach leaves out other solutions and because of this it has failed in several cases we have tried. Our approach is that of a multidimensional grid method, details of which will be given elsewhere.^{18,30} In brief, the function $F(\Delta, \omega_2, m)$ is calculated in every point of a $\{\Delta, \omega_2, m\}$ grid and its values are sorted towards the minimum, which is zero (as for a sum of squares). $F(\Delta, \omega_2, m)$ cannot be zero unless its three variables form a solution set for Eq. (44).

This approach allowed us to overcome the problems of the iterative approach (see above), for which it could also be used to provide good starting points towards all solutions. It can be shown, however,^{18,30} that with a modicum of desktop computing power a grid method can find all solutions with a precision greatly exceeding that afforded by experiment. A computer program to solve Eq. (44) has been written in Turbo C++ for DOS and run^{18,30} on an IBM PC compatible computer with a 386SX25 processor and a 387SX25 coprocessor. The data employed in the calculations are summarised in Table I and the results are given in Table II.

Referring to the linear non-Condon parameter m , to our

TABLE II. Calculated excited state^a parameters.

System	Calc. bond length change (pm)	Prev. calc. bond length change (pm)	Calc. upper electronic state vibrational wave number (cm ⁻¹)	Expt. upper electronic state vibrational wave number (cm ⁻¹)	Calc. linear non-Condon parameter <i>m</i>
TiL ₄ ^b	10.9	10.5	128	N/A	-0.03
KMnO ₄ :KClO ₄ ^c	4.4	4.6	747	740	0.00
K ₂ MnO ₄ ^d	5.0	4.4	740	750	-0.05
[NBu ₄] ₂ [WS ₄] ^e	11.0	5.8	413	410	-0.03
[NH ₄] ₂ [WS ₄] ^e	11.0	5.8	417	410	0.00
[NBu ₄] ₂ [MoS ₄] ^f	8.9	7.0	398	410	-0.07

^aRegarded as an unsplit ¹T₂ state in the present theoretical/experimental treatment.^bReference 31.^cReferences 21 and 24.^dReference 21.^eReferences 21 and 22.^fReferences 21 and 23.

knowledge this study is the first to take *m* into consideration in a practical, consistent way. The theory⁷⁻⁹ introduces non-Condon parameters and there has been an attempt³¹ to calculate *m* for TiL₄. The value of *m* = -0.3³¹ is, however, significantly greater than that (-0.1) acceptable for a linear non-Condon approximation [see Eqs. (19), (31b), and Appendix A]; our best fit value for *m* is -0.03.

The general equations (41a) and (41b) predict REPs for fundamentals and overtones using a single set of parameters. The fit is best illustrated for K[MnO₄] isomorphously diluted into K[ClO₄]^{21,24} [Figs. 1(a)–1(c)] for *m* = 0; the fit for *m* = -0.05 is significantly poorer. On the other hand, for [NBu₄]₂[MoS₄]²³ [Figs. 2(a), 2(b)] it is evident (despite the paucity of experimental points) that the fit for *m* = -0.07 is significantly better than for *m* = 0. The present calculated bond length changes for [WS₄]²⁻ and [MoS₄]²⁻ (8.9–11.0 pm) are larger than those previously reported for these ions (5.8–7.0 pm) on excitation to the lowest ¹T₂ state, but it is clear from Fig. 4 of Ref. 23 that the higher value would have given an equally good fit in the earlier analysis.

The high precision afforded by the theoretical calculations (see Table II) is restricted in practice by the experimental error. By varying the band intensities of the harmonics by 10% and comparing the resulting EPs, we found¹⁸ that the precision limits are ±0.5 pm for the bond length change and ±5 cm⁻¹ for the vibrational wave number of the upper state. Were the error in measuring the intensities of the RR harmonics only 5%, the precision would be closer to ±0.2 pm for the bond length change and ±2 cm⁻¹ for the vibrational wave number of the upper state.

Greater experimental accuracy could be achieved within the approach described in this paper; measuring the intensities of all four harmonics in the same spectrum, preferably using a multichannel spectrometer, eliminates time-dependent errors which would otherwise alter the observed band intensities. Numerical post-acquisition spectrum processing would further improve the accuracy of the integrated band intensities and hence of the calculated parameters. The method described here would provide then accurate, easy to obtain values for the parameters describing a molecule upon excitation, i.e., the bond length change and the vibrational

wave number of its resonant excited electronic state.

Our approach to using Eqs. (41) and (42) is by no means the only one possible. It has been adopted because in the examples selected each RR spectrum contained at least four harmonics. If this were not the case, as long as a resonance Raman spectrum is observed for each of three different excitation wavelengths (i.e., the spectrum shows the fundamental and first overtone bands), Eq. (43) can be written

$$\frac{\text{REP}_2(\omega_i)}{\text{REP}_1(\omega_i)} = \frac{|\alpha_2^{\text{NC}}(\omega_i)|^2}{|\alpha_1^{\text{NC}}(\omega_i)|^2}, \quad i = 1, 2, 3. \quad (45)$$

Equation (44) becomes then

$$F(\Delta, \omega_2, m) = \sum_{i=1}^3 \left[\left(\frac{|\alpha_2^{\text{NC}}(\omega_i, \Delta, \omega_2, m)|^2}{|\alpha_1^{\text{NC}}(\omega_i, \Delta, \omega_2, m)|^2} \right)_{\text{calculated}} - \left(\frac{\text{REP}_2(\omega_i)}{\text{REP}_1(\omega_i)} \right)_{\text{experimental}} \right]^2. \quad (46)$$

The procedure for minimising the function *F*(Δ, ω₂, *m*) and finding the parameters is the same as that described earlier.

It is necessary to remark about the solutions to Eqs. (43) and (45) that, while mathematically several solutions are possible (we have chosen our grid method for this reason), in most cases all but one of them are spurious. In some other cases it is not inconceivable to have more than one molecular configuration (i.e., several {Δ, ω₂, *m*} sets) which satisfy Eq. (43) and (45). Choosing the correct solution must then make use of further information such as, for example, comparison with similar molecular structures, examining relative bond length change and upper state frequency shift or conformity with the approximations of the method [Eqs. (31b)]. As stated in Sec. I, the problem can easily become overdetermined; if experimental data are available (i.e., a second RR spectrum), solving the system Eq. (43) for a different excitation frequency ω should also restrict the number of solutions.

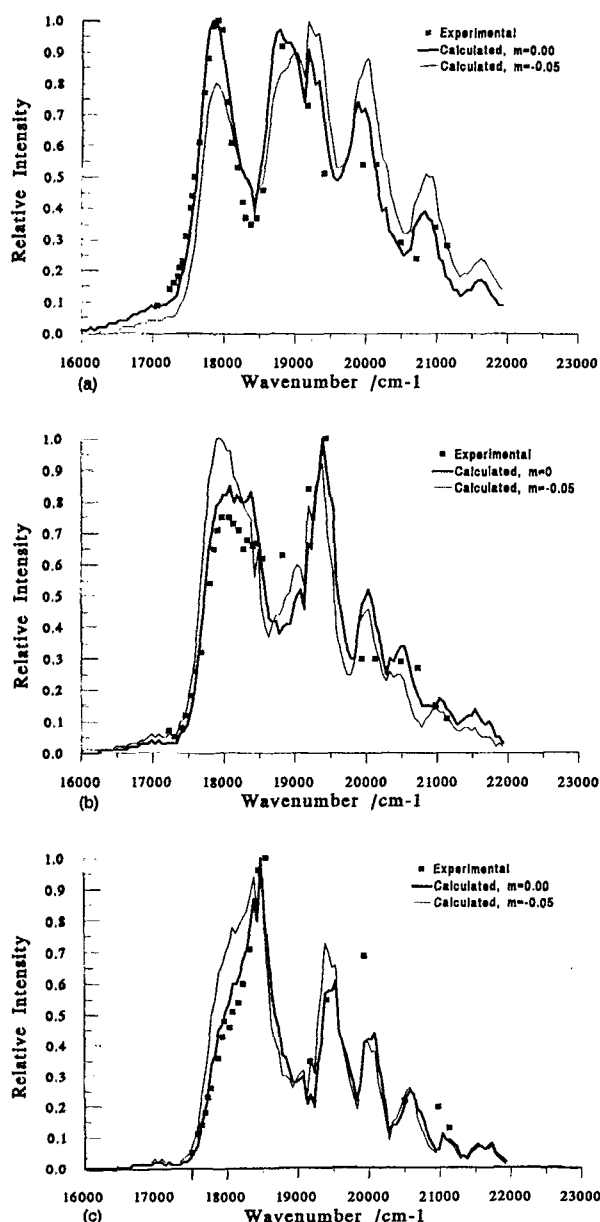


FIG. 1. Comparison of the experimental and calculated excitation profiles of the $\nu_1(a_1)$, $2\nu_1(a_1)$, and $3\nu_1(a_1)$ bands of the $[\text{MnO}_4]^-$ ion in a $\text{K}[\text{MnO}_4]/\text{K}[\text{ClO}_4]$ mixed crystal. The intensity reference is the $\nu_1(a_1)$ band of the $[\text{ClO}_4]^-$ ion. The data employed have been corrected for the spectral response of the spectrometer.

IV. CONCLUSIONS

The present model provides three vibronic parameters for fitting fundamental and overtone Raman excitation profiles, or for explaining the relative intensities of fundamental and overtone scattering excited at any one wavelength. The potential energy curve (Raman subspace) displacement parameter, Δ , has always been the essential parameter in the standard model for RRS. The wave number of the Raman mode in the upper potential energy curve ($\tilde{\nu}_2$), as distinct from that in the ground state ($\tilde{\nu}_1$), has been previously introduced by several workers as another parameter in RRS theory. The dependence of the transition moment on nuclear coordinate(s)—the non-Condon term—has also received

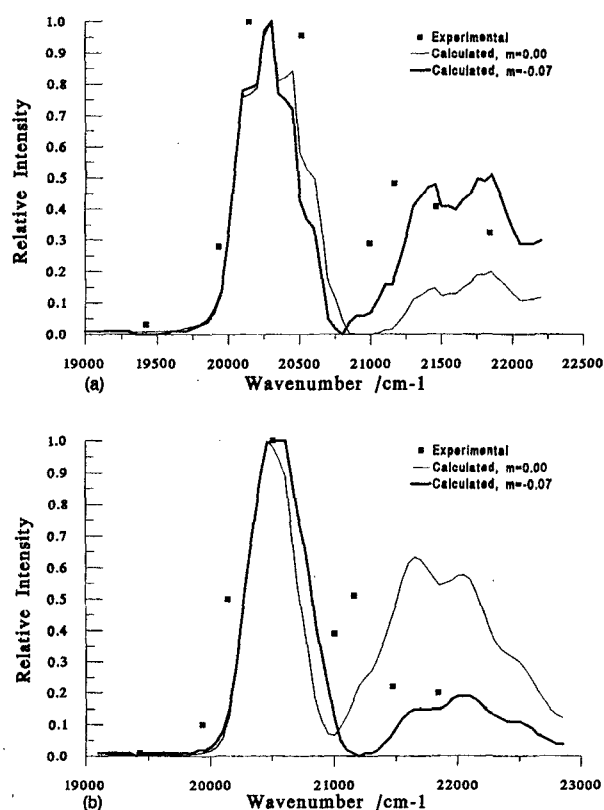


FIG. 2. Comparison of the experimental and calculated excitation profiles of the $\nu_1(a_1)$ and $2\nu_1(a_1)$ bands of the $[\text{MoS}_4]^{2-}$ ion in $[n\text{-Bu}_4\text{N}]_2[\text{MoS}_4]$, emphasising the influence of m (the linear non-Condon factor) on the quality of the fit.

some (but less) attention in the RRS scattering of fundamentals and typically at the linear level (parameter m). Here expressions are offered for n th order scattering (and the corresponding transform expressions) that simultaneously include all three vibronic parameters.

The formalism also separates the Raman subspace from the non-Raman space, thereby formally and implicitly including temperature dependence and energy dependent damping in the non-Raman space. The Raman space is treated only as one-dimensional (the coordinate of the Raman mode)—thus excluding Duschinsky rotation—and it is taken to be thermally unexcited. These appear to be realistic approximations for the six molecules that have been studied for each of which there is only a single totally symmetric fundamental and for which the vibrational quantum considerably exceeds the experimental kT . The trio of vibronic parameters ($\Delta, \tilde{\nu}_2, m$) are determined for each system. At no point are absolute Raman cross-sections required or used. The significance of these vibronic properties (and the consistently negative sign of m , when not zero) invite theoretical interpretation.

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APPENDIX A: THE n TH ORDER RR CORRELATOR FOR LINEAR NON-CONDON COUPLING ($\hbar\omega_1/kT \gg 1$)

The n th order RR correlator, A_n^{NC} [Eq. (23)], (and the corresponding NC matrix element $\langle 0|\hat{A}_n(1)\hat{M}\hat{B}\hat{M}\hat{C}|0\rangle$) is to be expressed in terms of the Condon correlator A_n^{C} (and the corresponding matrix element $\langle 0|\hat{A}_n(1)\hat{B}\hat{C}|0\rangle$) for which we have general expressions.¹² The linear non-Condon coupling operator (linear in nuclear displacement) is

$$\hat{M} \equiv 1 + m(\hat{a}_1 + \hat{a}_1^\dagger) \quad (\text{A1})$$

in which m is the dimensionless vibronically induced transition moment in units of the allowed transition moment. \hat{a}_1 and \hat{a}_1^\dagger are the raising and lowering (ket side) operators in the space of the ground state oscillator.

We proceed by first transforming \hat{M} into a function only of \hat{a}_2 and \hat{a}_2^\dagger , the raising and lowering operators for the harmonic potential of the excited electronic state. Then using commutation relationships from Appendix B, the second \hat{M} in the NC matrix element is passed through \hat{B} and the result is reconverted to a function of \hat{a}_1 and \hat{a}_1^\dagger , and together with the remaining \hat{M} the net operation is performed on the left upon $\hat{A}_n(1)$.

The general linear relationship between the two sets of raising and lowering operators of two harmonic potential energy (PE) curves 1 and 2 is

$$\hat{a}_2^\dagger = p + q\hat{a}_1^\dagger + r\hat{a}_1 \quad (\text{A2a})$$

with

$$\hat{a}_2 = p + q\hat{a}_1 + r\hat{a}_1^\dagger, \quad (\text{A2b})$$

where $\{p, q, r\}$ are dimensionless constants fixed by the Manneback relationships (see Appendix C). p relates to the displacement parameter for the two PE curves, q and r relate to the changes in their characteristic frequencies. Using Eqs. (A2a,b) in Eq. (A1) we find that

$$\hat{M} = 1 - \frac{2mp}{q+r} + \frac{m}{q+r} (\hat{a}_2^\dagger + \hat{a}_2). \quad (\text{A3})$$

Using Eqs. (B12a) and (B12b) we obtain

$$\hat{B}\hat{M} = \hat{B} \left(1 - \frac{2mp}{q+r} \right) + \frac{m}{q+r} (\hat{a}_2^\dagger e^{-i\tau\omega_2} + \hat{a}_2 e^{i\tau\omega_2}) \hat{B}. \quad (\text{A4})$$

But with Eqs. (A2) we obtain

$$\begin{aligned} \hat{B}\hat{M} = & \hat{B} \left[1 - \frac{2mp}{q+r} + \frac{mp}{q+r} (e^{-i\tau\omega_2} + e^{i\tau\omega_2}) \right] \\ & + m \left[\frac{q}{q+r} e^{-i\tau\omega_2} + \frac{r}{q+r} e^{i\tau\omega_2} \right] \hat{a}_1^\dagger \hat{B} \\ & + m \left[\frac{r}{q+r} e^{-i\tau\omega_2} + \frac{q}{q+r} e^{i\tau\omega_2} \right] \hat{a}_1 \hat{B}. \end{aligned} \quad (\text{A5})$$

With Eq. (A5) for $\hat{B}\hat{M}$ we construct $\langle 0|\hat{A}_n(1)\hat{M}\hat{B}\hat{M}\hat{C}|0\rangle$ as

$$\begin{aligned} \langle 0|\hat{A}_n(1)\hat{M}\hat{B}\hat{M}\hat{C}|0\rangle = & \left[1 + \frac{mp}{q+r} (e^{i\tau\omega_2} + e^{-i\tau\omega_2} - 2) \right] \langle 0|\hat{A}_n(1)\hat{B}\hat{C}|0\rangle + m \left(1 + \frac{q}{q+r} e^{i\tau\omega_2} + \frac{r}{q+r} e^{-i\tau\omega_2} \right) \\ & \times \langle 0|\hat{A}_{n+1}(1)\hat{B}\hat{C}|0\rangle + mn \left(1 + \frac{q}{q+r} e^{-i\tau\omega_2} + \frac{r}{q+r} e^{i\tau\omega_2} \right) \langle 0|\hat{A}_{n-1}(1)\hat{B}\hat{C}|0\rangle \end{aligned} \quad (\text{A6})$$

in which we have neglected all terms of order m^2 .

Equation (A6) leads directly to the NC expression for absorption by simply setting $n=0$ (with $\langle 0|\hat{A}_{-1}(1)\hat{B}\hat{C}|0\rangle \equiv 0$):

$$\begin{aligned} \langle 0|\hat{M}\hat{B}\hat{M}\hat{C}|0\rangle = & \left[1 + \frac{mp}{q+r} (e^{i\tau\omega_2} + e^{-i\tau\omega_2} - 2) \right] \\ & \times \langle 0|\hat{A}_0(1)\hat{B}\hat{C}|0\rangle + m \left(1 + \frac{q}{q+r} e^{i\tau\omega_2} \right. \\ & \left. + \frac{r}{q+r} e^{-i\tau\omega_2} \right) \langle 0|\hat{A}_1(1)\hat{B}\hat{C}|0\rangle. \end{aligned} \quad (\text{A7})$$

Equation (A6) also can be transformed into the n th order RR correlator using Eq. (23) to obtain Eq. (25)

$$\begin{aligned} A_n^{\text{NC}}(\tau) = & \left[1 + \frac{mp}{q+r} (e^{i\tau\omega_2} + e^{-i\tau\omega_2} - 2) \right] A_n^{\text{C}}(\tau) \\ & + m(n+1)^{1/2} \left(1 + \frac{q}{q+r} e^{i\tau\omega_2} + \frac{r}{q+r} e^{-i\tau\omega_2} \right) \\ & \times A_{n+1}^{\text{C}}(\tau) + mn^{1/2} \left(1 + \frac{q}{q+r} e^{-i\tau\omega_2} \right. \\ & \left. + \frac{r}{q+r} e^{i\tau\omega_2} \right) A_{n-1}^{\text{C}}(\tau). \end{aligned} \quad (\text{A8})$$

HT obtained the expression for $A_1^{\text{NC}}(\tau)$, the first-order Raman correlator with NC effects by proceeding in a different way. A (limited) temperature averaging was achieved through the appropriate Trace that includes the Boltzmann weighting operator. The cyclic permutation of operators (see HT and Appendix B) was used. Eq. (A8) at $n=1$ agrees with the HT

result only when $\omega_1 = \omega_2$ (or $r=0$). We choose to apply Eq. (A8) as our basic NC equation for n th order scattering.

APPENDIX B: COMMUTATION ALGEBRA

Here proofs are set forth of commutation rules that apply to the product and matrix elements of three operators important to this two-harmonic PE curve problem: an arbitrary function of the raising and lowering operators in the ground and excited states and the time evolution operators on each of these curves. Some of these properties are essential to the constructions presented in the HT work as well as to the material presented in Appendix A. Let us define the arbitrary function of raising and lowering operators as:

$$\hat{A} \equiv f(\hat{a}_1^\dagger, \hat{a}_1, \hat{a}_2^\dagger, \hat{a}_2) \quad (\text{B1a})$$

the propagator in the upper state as

$$\hat{B} \equiv e^{-i\tau H_2}, \text{eigenkets } \{|b\rangle\}, \text{eigenvalues } \{e^{-i\tau\omega_b}\} \quad (\text{B1b})$$

and the (inverse) propagator in the ground state as

$$\hat{C} \equiv e^{i\tau H_1}, \text{eigenkets } \{|c\rangle\}, \text{eigenvalues } \{e^{i\tau\omega_c}\}. \quad (\text{B1c})$$

(The earlier notational choice [Eqs. (7)] for the eigenkets of H_1 and H_2 , $\{|j_1\rangle\}$ and $\{|j_2\rangle\}$, is simplified here.)

We show that when $|i\rangle$ is a particular member of the ground state set $\{|c\rangle\}$ then

$$\langle i|\hat{C}\hat{A}\hat{B}|i\rangle = \langle i|\hat{A}\hat{B}\hat{C}|i\rangle = \langle i|\hat{C}\hat{B}\hat{A}^\dagger|i\rangle = \langle i|\hat{B}\hat{A}^\dagger\hat{C}|i\rangle, \quad (\text{B2a})$$

$$\langle i|\hat{C}\hat{B}\hat{A}|i\rangle = \langle i|\hat{B}\hat{A}\hat{C}|i\rangle = \langle i|\hat{C}\hat{A}^\dagger\hat{B}|i\rangle = \langle i|\hat{A}^\dagger\hat{B}\hat{C}|i\rangle, \quad (\text{B2b})$$

and

$$\langle i|\hat{A}\hat{C}\hat{B}|i\rangle = \langle i|\hat{B}\hat{C}\hat{A}^\dagger|i\rangle. \quad (\text{B2c})$$

We also know that under the trace (Tr) operation cyclic permutation of the operators is valid. For example

$$\text{Tr}\{\hat{A}\hat{B}\hat{C}\dots\} = \text{Tr}\{\hat{B}\hat{C}\dots\hat{A}\} = \text{Tr}\{\hat{C}\dots\hat{A}\hat{B}\}. \quad (\text{B3})$$

Finally, for the special case when $\hat{A} \equiv (\hat{a}_1^\dagger)^n \equiv \hat{A}_n^\dagger(1)$

$$\hat{A}_n^\dagger(1)\hat{C} = \hat{C}\hat{A}_n^\dagger(1)e^{-i\tau\omega_1} \quad (\text{B4a})$$

and when $\hat{A} \equiv (\hat{a}_2^\dagger)^n \equiv \hat{A}_n^\dagger(2)$

$$\hat{A}_n^\dagger(2)\hat{B} = \hat{B}\hat{A}_n^\dagger(2)e^{i\tau\omega_2} \quad (\text{B4b})$$

in which ω_2 and ω_1 are the (circular) frequencies of the two harmonic oscillators. Analogous relationships hold for $\hat{A}_n(1)\hat{C}$ and $\hat{A}_n(2)\hat{B}$.

PROOFS:

First, since H_1 and H_2 are Hermitian, we have

$$\hat{B}|b\rangle = e^{-i\tau\omega_b}|b\rangle \quad \text{and} \quad \langle b|\hat{B} = e^{-i\tau\omega_b}\langle b| \Leftrightarrow H_2|b\rangle = \omega_b|b\rangle, \quad (\text{B5a})$$

$$\hat{C}|c\rangle = e^{i\tau\omega_c}|c\rangle \quad \text{and} \quad \langle c|\hat{C} = e^{i\tau\omega_c}\langle c| \Leftrightarrow H_1|c\rangle = \omega_c|c\rangle. \quad (\text{B5b})$$

Now we can insert the identity operators $\sum_b|b\rangle\langle b|$ and $\sum_c|c\rangle\langle c|$ and, given Eqs. (B5), obtain for $|i\rangle$ a member of $\{|c\rangle\}$

$$\begin{aligned} \langle i|\hat{C}\hat{A}\hat{B}|i\rangle &= \sum_{b,c} \langle i|\hat{C}|c\rangle\langle c|\hat{A}|b\rangle\langle b|\hat{B}|i\rangle \\ &= \sum_{b,c} e^{-i\tau\omega_b} e^{i\tau\omega_i} (\langle i|c\rangle\langle c|\hat{A}|b\rangle\langle b|i\rangle). \end{aligned} \quad (\text{B6})$$

From Eq. (B6) we can reinsert $e^{i\tau\omega_i}$ on the ket side, properly close on the identity operators, to obtain

$$\langle i|\hat{C}\hat{A}\hat{B}|i\rangle = \sum_b \langle i|\hat{A}|b\rangle\langle b|e^{-i\tau\omega_b}e^{i\tau\omega_i}|i\rangle = \langle i|\hat{A}\hat{B}\hat{C}|i\rangle. \quad (\text{B7a})$$

On the other hand, provided \hat{A} is such that $\langle i|b\rangle\langle b|\hat{A}|c\rangle\langle c|i\rangle$ is pure real (and that is the case for all \hat{A} relevant to this problem) we have

$$\begin{aligned} (\langle i|c\rangle\langle c|\hat{A}|b\rangle\langle b|i\rangle) &= (\langle i|c\rangle\langle c|\hat{A}|b\rangle\langle b|i\rangle)^* \\ &= (\langle i|b\rangle\langle b|\hat{A}^\dagger|c\rangle\langle c|i\rangle) \end{aligned} \quad (\text{B7b})$$

and we can reassemble \hat{B} and \hat{C} in Eq. (B6) using Eq. (B5) and apply closure to obtain

$$\begin{aligned} \sum_{b,c} e^{-i\tau\omega_b} e^{i\tau\omega_i} (\langle i|c\rangle\langle c|\hat{A}|b\rangle\langle b|i\rangle) \\ = \sum_{b,c} e^{-i\tau\omega_b} e^{i\tau\omega_i} (\langle i|b\rangle\langle b|\hat{A}^\dagger|c\rangle\langle c|i\rangle) = \langle i|\hat{C}\hat{B}\hat{A}^\dagger|i\rangle \end{aligned} \quad (\text{B7c})$$

and

$$\sum_{b,c} e^{-i\tau\omega_b} e^{i\tau\omega_i} \langle i|c\rangle\langle c|\hat{A}|b\rangle\langle b|i\rangle = \langle i|\hat{B}\hat{A}^\dagger\hat{C}|i\rangle. \quad (\text{B7d})$$

Thus

$$\langle i|\hat{C}\hat{A}\hat{B}|i\rangle = \langle i|\hat{A}\hat{B}\hat{C}|i\rangle = \langle i|\hat{C}\hat{B}\hat{A}^\dagger|i\rangle = \langle i|\hat{B}\hat{A}^\dagger\hat{C}|i\rangle. \quad (\text{B2a})$$

Similar procedures lead to Eq. (B2b). Equation (B2c) follows using the reality of $(\langle i|\hat{A}|b\rangle\langle b|c\rangle\langle c|i\rangle)$, similar to Eq. (B7b).

Next we consider the special cases where

$$\hat{A} \equiv \hat{a}_1^n \equiv \hat{A}_n(1), \quad \text{or} \quad (\hat{a}_1^\dagger)^n \equiv \hat{A}_n^\dagger(1) \quad (\text{B8a})$$

or

$$\hat{A} \equiv \hat{a}_2^n \equiv \hat{A}_n(2), \quad \text{or} \quad (\hat{a}_2^\dagger)^n \equiv \hat{A}_n^\dagger(2). \quad (\text{B8b})$$

For the raising and lowering operators we have for the ground state 1

$$\hat{a}_1^n|c\rangle = C_c^{(-n)}|c-n\rangle, \quad (\hat{a}_1^\dagger)^n|c\rangle = C_c^{(n)}|c+n\rangle \quad (\text{B9a})$$

and in conjugate form,

$$\langle c|(\hat{a}_1^\dagger)^n = C_c^{(-n)}\langle c-n|, \quad \langle c|\hat{a}_1^n = C_c^{(n)}\langle c+n|. \quad (\text{B9b})$$

Similarly for the excited state 2

$$\hat{a}_2^n|b\rangle = C_b^{(-n)}|b-n\rangle, \quad (\hat{a}_2^\dagger)^n|b\rangle = C_b^{(n)}|b+n\rangle \quad (\text{B9c})$$

and in conjugate form

$$\langle b|(\hat{a}_2^\dagger)^n = C_b^{(-n)}\langle b-n|, \quad \langle b|\hat{a}_2^n = C_b^{(n)}\langle b+n|. \quad (\text{B9d})$$

Thus we have

$$\begin{aligned}\hat{A}_n(1)\hat{C} &= \sum_c \hat{A}_n(1)|c\rangle\langle c|\hat{C} \\ &= \sum_c C_c^{(-n)}|c-n\rangle\langle c|e^{i\tau\omega_c} \\ &= \hat{C}\sum_c (C_c^{(-n)}|c-n\rangle\langle c|)e^{i\tau\omega_i} \\ &= \hat{C}\hat{A}_n(1)e^{i\tau\omega_i}.\end{aligned}\quad (\text{B10a})$$

Similarly

$$\begin{aligned}\hat{A}_n^\dagger(1)\hat{C} &= \sum_c \hat{A}_n^\dagger(1)|c\rangle\langle c|\hat{C} \\ &= \sum_c C_c^{(n)}|c+n\rangle\langle c|e^{i\tau\omega_c} \\ &= \hat{C}\sum_c (C_c^{(n)}|c+n\rangle\langle c|)e^{-i\tau\omega_i} \\ &= \hat{C}\hat{A}_n^\dagger(1)e^{-i\tau\omega_i}\end{aligned}\quad (\text{B10b})$$

which is just Eq. (B4a).

Likewise for

$$\begin{aligned}\hat{A}_n(2)\hat{B} &= \sum_b \hat{A}_n(2)|b\rangle\langle b|\hat{B} \\ &= \sum_b C_b^{(-n)}|b-n\rangle\langle b|e^{-i\tau\omega_b} \\ &= \hat{B}\sum_b (C_b^{(-n)}|b-n\rangle\langle b|)e^{-i\tau\omega_2} \\ &= \hat{B}\hat{A}_n(2)e^{-i\tau\omega_2},\end{aligned}\quad (\text{B11a})$$

and similarly

$$\begin{aligned}\hat{A}_n^\dagger(2)\hat{B} &= \sum_b \hat{A}_n^\dagger(2)|b\rangle\langle b|\hat{B} \\ &= \sum_b C_b^{(n)}|b+n\rangle\langle b|e^{-i\tau\omega_b} \\ &= \hat{B}\sum_b (C_b^{(n)}|b+n\rangle\langle b|)e^{i\tau\omega_2} \\ &= \hat{B}\hat{A}_n^\dagger(2)e^{i\tau\omega_2}\end{aligned}\quad (\text{B11b})$$

which is just Eq. (B4b).

The special case for $n=1$ in Eqs. (B11a) and (B11b), needed in Appendix A, becomes

$$\hat{a}_2 e^{-i\tau H_2} = e^{-i\tau\omega_2} e^{-i\tau H_2} \hat{a}_2 \quad (\text{B12a})$$

and

$$\hat{a}_2^\dagger e^{-i\tau H_2} = e^{i\tau\omega_2} e^{-i\tau H_2} \hat{a}_2^\dagger. \quad (\text{B12b})$$

In general, Eqs. (B10) and (B11) can be used with Eq. (B2) to recover several useful identities such as

$$\begin{aligned}\langle i|\hat{B}\hat{A}_n(1)\hat{C}|i\rangle &= e^{-i\tau\omega_i}\langle i|\hat{B}\hat{C}\hat{A}_n(1)|i\rangle \\ &= \langle i|\hat{C}\hat{A}_n^\dagger(1)\hat{B}|i\rangle = e^{i\tau\omega_i}\langle i|\hat{A}_n^\dagger(1)\hat{C}\hat{B}|i\rangle.\end{aligned}\quad (\text{B13})$$

APPENDIX C: THE MANNEBACK EQUATIONS AND THE LINK BETWEEN THE PARAMETERS

The parameters $\{p, q, r\}$ found in the linear relationship between the raising and lowering operators of the excited (2) and ground state (1) harmonic PE curves need to be related to the two characteristic frequencies ω_1 and ω_2 and the relative displacement, Δ , of the minima of the two curves [$\Delta = R_e(2) - R_e(1)$]. In 1951 Manneback (M)³² published key recurrence equations relating the Franck–Condon amplitudes between two harmonic PE curves that have different characteristic frequencies ω_1 and ω_2 and displaced minima. The two “fundamental formulas,” called I and II in (M), are given in our bra/ket notation (Appendix B)

$$\begin{aligned}\langle b+1|c\rangle &= \frac{1}{(b+1)^{1/2}} [-b^{1/2}\mathbf{k}_M\langle b-1|c\rangle \\ &\quad + c^{1/2}\mathbf{k}_M^+\langle b|c-1\rangle - \mathbf{a}_M\langle b|c\rangle]\end{aligned}\quad (\text{I})$$

and

$$\begin{aligned}\langle b|c+1\rangle &= \frac{1}{(c+1)^{1/2}} [c^{1/2}\mathbf{k}_M\langle b|c-1\rangle \\ &\quad + b^{1/2}\mathbf{k}_M^+\langle b-1|c\rangle + \mathbf{b}_M\langle b|c\rangle].\end{aligned}\quad (\text{II})$$

The parameters, directly from (M), are in bold face and subscripted by “M”. Eqs. (2) and (3) of Ref. 32 relate these to a measure of the displacement, M , and the two frequencies according to

$$\begin{aligned}\mathbf{a}_M &= M \left[\frac{2\omega_1}{(\omega_1 + \omega_2)} \right]^{1/2}, \quad \mathbf{b}_M = M \left[\frac{2\omega_2}{(\omega_1 + \omega_2)} \right]^{1/2}, \\ \mathbf{k}_M^+ &= \frac{2(\omega_1\omega_2)^{1/2}}{(\omega_1 + \omega_2)}, \quad \mathbf{k}_M = \frac{(\omega_1 - \omega_2)}{(\omega_1 + \omega_2)}.\end{aligned}\quad (\text{C1})$$

The dimensionless displacement parameter, M , is further defined in terms of the actual difference in the location of the harmonic oscillator minima $\Delta = R_e(2) - R_e(1)$

$$M = \frac{\Delta}{\lambda},$$

where

$$\lambda = \left(\frac{h}{2\pi\mu} \right)^{1/2} \left(\frac{\omega_1 + \omega_2}{\omega_1\omega_2} \right)^{1/2}. \quad (\text{C2})$$

Here μ is the reduced mass of the oscillator and the reference distance, λ , is the square root of the average of the mean square displacements of the oscillators in the two potentials. For practical use we choose the units of Δ to be picometers (pm), those of the wave number [$\tilde{\nu} = \omega/(2\pi c)$] to be cm^{-1} and those of μ to be atomic mass units (amu) to give

$$M = 1.722\ 211\ 5 \times 10^{-3} \mu^{1/2} \Delta \left(\frac{\tilde{\nu}_1 \tilde{\nu}_2}{\tilde{\nu}_1 + \tilde{\nu}_2} \right)^{1/2}. \quad (\text{C3})$$

We proceed to generate (I) and (II) using Eq. (A2) and thereby link our $\{p, q, r\}$ parameters to those of M and thus relate $\{p, q, r\}$ to $\{\omega_1, \omega_2, \Delta\}$. Given that

$$\hat{a}_2^\dagger = p + q\hat{a}_1^\dagger + r\hat{a}_1, \quad \hat{a}_2 = p + q\hat{a}_1 + r\hat{a}_1^\dagger \quad (\text{C4})$$

and with $\{|b\rangle\}$ the eigenkets of H_2 we have

$$\hat{a}_2^\dagger |b\rangle = (b+1)^{1/2} |b+1\rangle, \quad \text{and} \quad \langle b | \hat{a}_2 = (b+1)^{1/2} \langle b+1|, \\ \hat{a}_2 |b\rangle = (b)^{1/2} |b-1\rangle, \quad \text{and} \quad \langle b | \hat{a}_2^\dagger = b^{1/2} \langle b-1| \quad (\text{C5a})$$

and similarly with $\{|c\rangle\}$ the eigenkets of H_1 ,

$$\hat{a}_1^\dagger |c\rangle = (c+1)^{1/2} |c+1\rangle, \quad \text{and} \quad \langle c | \hat{a}_1 = (c+1)^{1/2} \langle c+1|, \\ \hat{a}_1 |c\rangle = (c)^{1/2} |c-1\rangle, \quad \text{and} \quad \langle c | \hat{a}_1^\dagger = (c)^{1/2} \langle c-1|. \quad (\text{C5b})$$

We can write now

$$\langle b | a_2 | c \rangle = (b+1)^{1/2} \langle b+1 | c \rangle \\ = \langle b | (p + q\hat{a}_1 + r\hat{a}_1^\dagger) | c \rangle \\ = p \langle b | c \rangle + c^{1/2} q \langle b | c-1 \rangle + (c+1)^{1/2} r \langle b | c+1 \rangle \quad (\text{C6})$$

or, upon rearrangement,

$$\langle b+1 | c \rangle = \frac{1}{(b+1)^{1/2}} [p \langle b | c \rangle + c^{1/2} q \langle b | c-1 \rangle \\ + (c+1)^{1/2} r \langle b | c+1 \rangle]. \quad (\text{C7})$$

Similarly

$$\langle b | a_2^\dagger | c \rangle = b^{1/2} \langle b-1 | c \rangle = \langle b | (p + q\hat{a}_1^\dagger + r\hat{a}_1) | c \rangle = p \langle b | c \rangle \\ + (c+1)^{1/2} q \langle b | c+1 \rangle + c^{1/2} r \langle b | c-1 \rangle. \quad (\text{C8})$$

From Eq. (C8) we can isolate $\langle b | c+1 \rangle$ and obtain Eq. (II') with our parameters:

$$\langle b | c+1 \rangle = \frac{1}{(c+1)^{1/2}} \left[b^{1/2} \left(\frac{1}{q} \right) \langle b-1 | c \rangle - c^{1/2} \left(\frac{r}{q} \right) \right. \\ \left. \times \langle b | c-1 \rangle - \left(\frac{p}{q} \right) \langle b | c \rangle \right]. \quad (\text{II}')$$

Comparing coefficients of like terms in Eqs. (II) and (II') we find

$$\mathbf{b}_M = - \left(\frac{p}{q} \right), \quad \mathbf{k}_M^+ = \left(\frac{1}{q} \right), \quad \mathbf{k}_M = - \left(\frac{r}{q} \right). \quad (\text{C9a})$$

Now we can obtain Eq. (I') by eliminating $\langle c | b+1 \rangle$ in Eq. (C7) using Eq. (II'). Thus

$$\langle b+1 | c \rangle = \frac{1}{(b+1)^{1/2}} \left[p \left(\frac{q-r}{q} \right) \langle b | c \rangle + c^{1/2} \left(\frac{q^2-r^2}{q} \right) \right. \\ \left. \times \langle b | c-1 \rangle + b^{1/2} \left(\frac{r}{q} \right) \langle b-1 | c \rangle \right]. \quad (\text{I}')$$

By comparing coefficients of like terms in Eqs. (I) and (I') we find

$$\mathbf{a}_M = -p \left(\frac{q-r}{q} \right), \quad \mathbf{k}_M^+ = \left(\frac{q^2-r^2}{q} \right), \quad \mathbf{k}_M = - \left(\frac{r}{q} \right). \quad (\text{C9b})$$

Equations (C9) are consistent and with Eq. (C1) lead, finally, to

$$p = -M \left[\frac{(\omega_2 + \omega_1)}{2\omega_1} \right]^{1/2}, \\ q = \frac{(\omega_2 + \omega_1)}{2(\omega_2 \omega_1)^{1/2}}, \quad (\text{C10}) \\ r = \frac{(\omega_2 - \omega_1)}{2(\omega_2 \omega_1)^{1/2}}$$

and with Eq. (C3),

$$p = -1.217\ 787\ 4 \times 10^{-3} \mu^{1/2} \tilde{\nu}_2^{1/2} \Delta. \quad (\text{C11})$$

¹ J. B. Page, in *Topics in Applied Physics*, Vol. 68 (Springer, Berlin, 1991), pp. 17–72.

² V. V. Hizhnyakov and I. Tehver, *Phys. Status Solidi* **21**, 755 (1967).

³ D. L. Tonks and J. B. Page, *Chem. Phys. Lett.* **79**, 247 (1981).

⁴ H. M. Lu and J. B. Page, *Chem. Phys. Lett.* **131**, 87 (1986).

⁵ H. M. Lu and J. B. Page, *J. Chem. Phys.* **88**, 3508 (1988).

⁶ H. M. Lu and J. B. Page, *J. Chem. Phys.* **90**, 5315 (1989).

⁷ I. J. Tehver, *Opt. Commun.* **38**, 279 (1981).

⁸ B. R. Stallard, P. M. Champion, P. R. Callis, and A. C. Albrecht, *J. Chem. Phys.* **78**, 712 (1983).

⁹ C. K. Chan, *J. Chem. Phys.* **81**, 1614 (1984).

¹⁰ P. M. Champion and A. C. Albrecht, *Chem. Phys. Lett.* **82**, 410 (1981).

¹¹ J. Cable and A. C. Albrecht, *J. Chem. Phys.* **84**, 1969 (1986).

¹² V. Hizhnyakov and I. Tehver, *J. Raman Spectrosc.* **19**, 383 (1988).

¹³ J. R. Cable and A. C. Albrecht, *J. Chem. Phys.* **84**, 4745 (1986).

¹⁴ A. C. Albrecht, *J. Chem. Phys.* **34**, 1476 (1961), and references therein.

¹⁵ Pusheng Li and P. M. Champion, *J. Chem. Phys.* **88**, 761 (1988).

¹⁶ C. K. Chan and J. B. Page, *J. Chem. Phys.* **79**, 5234 (1983).

¹⁷ C. K. Chan and J. B. Page, *Chem. Phys. Lett.* **104**, 609 (1984).

¹⁸ D. Oprea, PhD thesis, University of London, 1994.

¹⁹ R. J. H. Clark and P. D. Mitchell, *J. Am. Chem. Soc.* **95**, 8300 (1973).

²⁰ R. J. H. Clark and T. J. Dines, *J. Chem. Soc. Faraday Trans. 2* **78**, 723 (1982).

²¹ R. J. H. Clark, T. J. Dines, and J. M. Doherty, *Inorg. Chem.* **24**, 2088 (1985).

²² R. J. H. Clark, T. J. Dines, and G. P. Proud, *J. Chem. Soc. Dalton Trans.* **2019** (1983).

²³ R. J. H. Clark, T. J. Dines, and M. L. Wolf, *J. Chem. Soc. Faraday Trans. 2* **78**, 679 (1982).

²⁴ R. J. H. Clark and B. Stewart, *J. Am. Chem. Soc.* **103**, 6593 (1981); T. J. Dines, *Spectrochim. Acta A* **44**, 1087 (1988).

²⁵ D. L. Tonks and J. B. Page, *J. Chem. Phys.* **76**, 5820 (1982).

²⁶ B. Khodadoost, S. A. Lee, J. B. Page, and R. C. Hanson, *Phys. Rev. B* **38**, 5288 (1988).

²⁷ H. M. Lu and J. B. Page, *J. Chem. Phys.* **92**, 7038 (1990).

²⁸ Y. Gu and P. M. Champion, *Chem. Phys. Lett.* **171**, 254 (1990).

²⁹ J. M. Ortega and W. C. Rheinboldt, *Iterative Solution of Nonlinear Equations in Several Variables* (Academic, London, 1970).

³⁰ D. Oprea (in preparation).

³¹ M. C. C. Ribeiro, W. J. Barreto, M. L. A. Temperini, and P. S. Santos, *J. Phys. Chem.* **97**, 12153 (1993).

³² C. Manneback, *Physica* **17**, 1001 (1951).