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Application of Time-Dependent Raman Theory  
to the Analysis of Inorganic Photosystems \*

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1 Introduction

Recent developments by HELLER and coworkers [1] in the time-dependent theory of Raman scattering are of enormous potential value in determining structural and vibrational parameters in excited electronic states. Ground-state Raman intensities of fundamentals, overtones and combinations under resonance or near-resonance conditions can be used to determine normal coordinate displacements, force-constant changes and Duschinsky rotation in the excited state. This approach to excited-state characterization is particularly attractive because it does not require the direct observation of excited-state vibrational frequencies by TRVS or resolved vibronic spectroscopies. Thus, it is not hampered by short excited-state lifetimes and/or stringent experimental conditions. Furthermore, for systems where TRVS or vibronic data are available, Heller's theory affords an additional test of the accuracy of calculated excited-state parameters.

Continuing interest in elucidating the structure in the reactive excited state(s) of inorganic photosystems has prompted a re-examination of Heller's theory [2]. The aim has been to extend existing mathematical treatments to the more general (and commonly encountered) case in which coordinate displacements, force-constant changes and Duschinsky rotation occur simultaneously in the excited states. The most significant result of this work is the discovery of additional terms which were not explicitly developed in earlier treatments [1]. These new terms can make significant contributions to the scattering intensities of overtones and combinations. However, the broader implication is that attempts to obtain accurate excited-state structural information from ground-state Raman intensities will require consideration of all terms which can contribute to these intensities.

As demonstrated here, application of this more general formulation of Heller's theory to the analysis of real (and realistically obtainable) data is straightforward. As examples of the ease and utility of such analyses, attention is focused on some transition metal dimers whose photochemical and photophysical properties continue to be of considerable interest.

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## 2 Theory, Results and Discussion

The time-dependent expression for the polarizability is [1]

$$\alpha_{f,i}(\omega_I) = \int_0^{\infty} \exp [ i(\omega_I + E_i)t - \gamma t ] \langle \Psi_f | \Psi_i(t) \rangle dt + \text{NRT.} \quad (1)$$

The central problem thus lies in calculating the time-dependent overlap between the final scattering state,  $\Psi_f$ , and the wave packet,  $\Psi_i(t)$ , propagating on the excited-state potential energy surface. Assuming harmonic ground- and excited-state surfaces and a gaussian form for  $\Psi_i(t)$ , this problem can be treated classically for short propagation times. This leads to expressions for the polarizabilities which are complex polynomials in time containing the desired excited-state structural parameters (vide infra). All terms in these polynomials are complex so that modulus squaring of  $\alpha_{f,i}$  to obtain the scattering intensity does not result in any cancellations of cross-terms. These cross-terms are the ones not explicitly developed previously [1] but which can significantly influence the total intensity of overtones and combinations.

The complete expressions for the fundamental (2) and first overtone (3) in mode  $k$  are;

$$|\alpha_{1,0}|^2 = (2\omega_{0k})^{-1} (V_k^2 / \sigma^4) \epsilon_1(\beta) \quad (2)$$

$$|\alpha_{2,0}|^2 = (8\omega_{0k}^2)^{-1} [ (V_k^4 / \sigma^6) \epsilon_2(\beta) + ((\omega_{0k}^2 - V_{kk})^2 / \sigma^4) \epsilon_1(\beta) + (V_k^2 (\omega_{0k}^2 - V_{kk}) / \sigma^5) c'_{2,1}(\beta) ] \quad (3)$$

where  $V_k$  is the first derivative with respect to  $q_k$  of the excited-state surface in the Franck-Condon region and  $V_{kk}$  is the second derivative corresponding to the excited-state force constant. Thus  $\omega_{0k}^2 - V_{kk}$  is the change in force constant between ground and excited states. The  $\epsilon(\beta)$  are integral expressions describing the evolution of the wave packet (thus the overlap) on the excited-state surface at a point in the absorption envelope given by  $\beta = (\omega_I - E)/\sigma$  and  $2\sigma^2$  corresponds to the vibronic contribution to the absorption linewidth from totally symmetric modes. The integral expressions are plotted in Fig. 1. The contribution from  $c'_{2,1}$  results from the cross-term described above. It is apparent that as excitation is detuned from exact resonance this new term will significantly effect the overtone intensity in totally symmetric modes for which there is a change in force constant in the excited state. Note also that the influence of this term is strongly excitation wavelength dependent. An expression similar to (3) results for combination scattering intensity but involves the Duschinsky rotation term in place of the force constant change [2].

Equations (2) and (3) reveal the means for calculating the desired excited-state parameters. If fundamental and first overtone Raman intensities are available,  $2\sigma^2$  can be estimated from the absorption spectrum and the excited-state force constant,  $V_{kk}$ , and displacement,  $\Lambda_k = V_k/V_{kk}$ , can be obtained. Alternatively, IR or vibronic data can be used in place of overtone intensities to estimate  $V_{kk}$ . However, as illustrated in Fig. 1, if overtone intensities are used, the cross-term contribution cannot be neglected or erroneous  $V_{kk}$  values result. In addition, estimates of  $\Lambda_k$

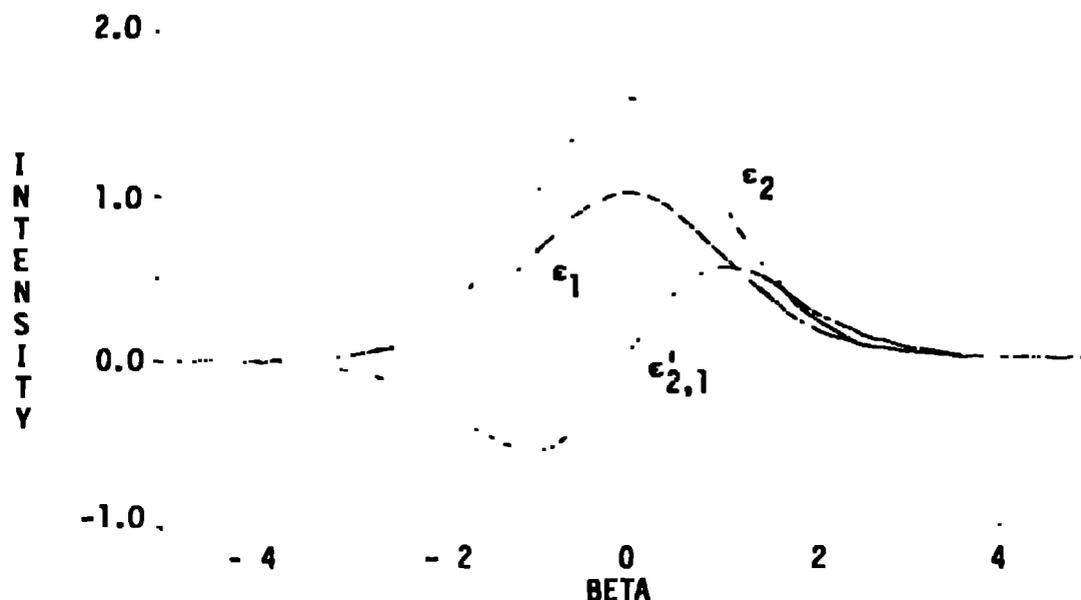


Figure 1. Time-dependent integral expressions in the generalized Heller theory

based solely on fundamental intensities will be in error when any appreciable change in force constant occurs.

To illustrate these points, calculations have been made for a number of quadruply bonded metal dimers. The characteristic features in these systems are a lowest-lying metal-localized  $\delta$ - $\delta^*$  electronic transition which reduces the bond order to three in the excited state and a ground-state vibrational mode comprised almost entirely of metal-metal stretching which is strongly resonance enhanced in the  $\delta$ - $\delta^*$  region. The results are summarized in Table 1. In all cases the vibrational frequency decreases and the bond length increases (3-8% elongation) in the excited state, both expected results for systems with a decreased excited-state bond order. The result for  $\text{Mo}_2(\text{O}_2\text{CCl}_3)_4$  warrant further consideration because the excited-state displacement has been determined previously by alternate means. Most notably, a simplified Heller theory analysis in which the change in force constant was neglected yielded  $\Delta = 0.045\text{\AA}$  [7]. Explicit inclusion of this term (Table 1) results in a 50% increase in the value of the displacement, clearly illustrating the importance of considering all factors when calculating excited-state parameters. A Frank-Condon analysis of the vibronic spectrum [3] gave  $\Delta = 0.1\text{\AA}$  for the acetate dimer suggesting that some discrepancies between time-dependent theory and FC analyses exist and remain to be resolved.

Table 1. Excited-state displacements in the metal stretching mode in metal dimers

	$\omega_{gs} [\text{cm}^{-1}]$	$\omega_{es} [\text{cm}^{-1}]$	$\Delta [\text{\AA}]$
$\text{Mo}_2(\text{O}_2\text{CCl}_3)_4$	395	355 <sup>a</sup>	0.07
$\text{Mo}_2\text{Cl}_8^{4-}$	346	336 <sup>b</sup>	0.15
$\text{Re}_2\text{Cl}_8^{2-}$	274	248 <sup>c</sup> , 258 <sup>c</sup>	0.13, 0.12
$\text{Re}_2\text{Br}_8^{2-}$	275	255 <sup>d</sup>	0.17

from vibronic absorption spectrum; <sup>a</sup>Ref.3 <sup>b</sup>Ref.4 <sup>c</sup>Ref.5 <sup>d</sup>Ref.6. <sup>e</sup>From Heller theory analysis of the overtone intensities.

### 3 Conclusions

The more general formulation of Heller's theory outlined here and in more detail elsewhere [2] should make it possible to characterize the excited states of real and chemically interesting systems with a high degree of reliability provided care is exercised in considering the influence of all factors in determining the scattering dynamics. The reliance of this method on ground-state Raman intensities makes it particularly convenient and a valuable complement to the more direct but often experimentally prohibitive methods such as TRVS. While further testing of the predictions of this formalism is required, preliminary results as presented here are encouraging.

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