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Continuum resonance Raman scattering of light by diatomic molecules. I. The role of radiative crossings between the potentials of the dressed molecule[a]

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Usual scattering theory only provides a formal result for continuum resonance Raman scattering amplitudes, leaving the task of evaluating numerically these amplitudes. We look instead, in the case of a diatomic molecule, for a system of coupled equations patterned after those of molecular collision theory which can provide them directly (i.e., numerically). These equations emphasize the role of radiative crossings between the potential curves of the dressed molecule (molecule in its initial electronic state with the incoming photon, in its intermediate state with no photon, in its final state with the outgoing photon). The channels involve the potentials of the dressed molecule plus two artificial entrance and exit channels coupled in such a way as to yield the Raman scattering amplitudes through the analysis of one of the elements of the scattering matrix. Electronic transition moments depending on the internuclear distance are easily introduced into the formalism. In order to test the numerical accuracy of this method it is possible to use an analytically exact formula valid for harmonic and linear potentials. It is shown that a three-figure accuracy is easily achieved. Comparisons are also made with the results of a semiclassical procedure based on an Airy representation of the Franck–Condon amplitudes. This method, which is used abundantly in the next paper, has the advantage of providing a very fast way of reaching the scattering amplitudes and gives an error which generally does not exceed a few percent.

I. INTRODUCTION

Continuum resonance Raman scattering is now a well-established method for the determination of the repulsive part of the potential curves of the excited states of diatomic molecules.[1] Although most of the studies have been so far performed for practical reasons on halogen molecules, it is to be expected that in the near future many other diatomic molecules will be amenable to experimental investigation by this technique when laser frequencies in the appropriate range are available.

The determination of molecular electronic potential curves from resonance Raman scattering data requires the theoretical evaluation of the scattering amplitudes from some assumed potentials which may then be subjected to an adjustment so as to fit the experimentally observed profiles. Several such studies have appeared recently.[2,3] The main problem in this context is the evaluation of a complex integral [Eq. (39) below] with an integrand depending on Franck–Condon amplitudes. Although several methods providing this integral have been described in the literature,[2,4] the numerical reliability of these estimates has not been stated.

This paper develops a procedure that we have recently briefly described.[5] This method provides near exact results against which any approximate determination can be evaluated. Centrifugal energies and varying electronic transition moments can be introduced easily into the scheme. Accuracy of this method based on the resolution of a system of coupled equations can be tested by using an analytical formula which is exact for the case of harmonic and linear potentials. We also make some tests for a semiclassical procedure which has the advantage of providing the amplitudes in a very simple way. Both coupled channel and semiclassical procedures will be used in the next paper to study the $\Delta n = 1$ profiles of Br_2.

This paper is organized as follows: in Sec. II, we recall that although Raman scattering may be viewed as a collision with photons being involved, application of formal scattering theory leads only a literal result, but not to a numerical estimate of the scattering cross section. However, as shown in Sec. III, we may, by the introduction of some additional artificial channels, as suggested in a different context by Shapiro,[6] obtain a set of coupled equations with a scattering matrix containing the information which is being looked for (i.e., the scattering amplitude). These coupled equations emphasize the role of radiative crossings which are made possible between molecular potential curves by the consideration of the photon energies. The equations can be somewhat simplified, as pointed out in Sec. III, where a reduced set of coupled equations is shown to lead to the evaluation of the vibrational parts of the amplitudes. Section IV describes the exact analytical formula corresponding to harmonic and linear potentials, as well as the semiclassical expressions based on an Airy representation of the Franck–Condon amplitudes. An example with harmonic and linear potentials is used to establish the accuracy of the coupled channel method and to estimate the reliability of the semiclassical model. Finally, in Sec. V we comment on some numerical aspects of the coupled channel procedure.

II. COLLISION THEORY AND CONTINUUM RESONANCE RAMAN SCATTERING

Raman scattering may be viewed as a collision with a photon hitting the molecule and a photon leaving it. Because the molecule changes its internal state, the scattering is accompanied by a change in frequency of the photon (inelastic collision). It is possible to give a solution of this problem using the tools of scattering theory,[7] but as we shall see below this does not lead in a direct manner to a practical way of calculating the Raman scattering probability.

In order to describe this collision one may use as an initial ket $|\psi_i\rangle$ a direct product of the initial molecular eigenket $|i\rangle$ of energy E_i by a one photon state of given wave vector k_0'' and polarization e_λ, that is,

$$|\psi_i\rangle = |i; k_0'', e_\lambda\rangle . \qquad (1)$$

The final state $|\psi_f\rangle$ with the molecule in state $|f\rangle$ with energy E_f and a photon described by $|k_0', e_\mu\rangle$ is

$$|\psi_f\rangle = |f; k_0', e_\mu\rangle . \qquad (2)$$

The transition probability to this state is given by

$$P_{fi} = |\langle \psi_f | S | \psi_i \rangle|^2 , \qquad (3)$$

where the scattering operator S is related to the transition operator T by

$$S = 1 - i\pi T . \qquad (4)$$

Energy conservation requires that $\hbar c |k_0''| - \hbar c |k_0'| = E_f - E_i$. The complete Hamiltonian of the system is written

$$\mathcal{H} = H_M + H_F + \mathcal{V} = \mathcal{H}_0 + \mathcal{V} , \qquad (5)$$

where H_M and H_F are the molecular and field Hamiltonians and $\mathcal{V}$ the molecule–field coupling. The operator T can be obtained from

$$T = \mathcal{V} + \mathcal{V} G \mathcal{V} , \qquad (6)$$

where G is the Green function $\lim_{\epsilon \to 0^+}(z - \mathcal{H})^{-1}$ with $z = \overline{E} + i\epsilon$, $\overline{E}$ being the collision energy $E_i + \hbar c |k_0''|$. To lowest order in $\mathcal{V}$ it is possible to use in Eq. (6) $G_0 = \lim_{\epsilon \to 0^+}(z - \mathcal{H}_0)^{-1}$ in place of G. This amounts physically to (a) retaining only as intermediate states in the scattering those states which are simultaneously coupled to $|\psi_i\rangle$ and $|\psi_f\rangle$; (b) neglecting shifts and widths of possible intermediate discrete levels.

We take for $\mathcal{V}$ the coupling of the molecular electric dipole operator d to the electric field at the origin[8]

$$\mathcal{V} = -i \sum_{k,\sigma} \sqrt{\frac{\hbar \omega_k}{2\epsilon_0 L^3}} \, d \cdot e_\sigma [a_{k,\sigma} - a_{k,\sigma}^\dagger] , \qquad (7)$$

where $\omega_k = c|k|$; $a_{k,\sigma}$ and $a_{k,\sigma}^\dagger$ are the annihilation and creation operator of photon k, σ, L is the dimension of the box used in quantizing the field.

Let us assume that $|e E\eta; \text{vac}\rangle$ represents a continuum of excited molecular states belonging to electronic state e with no photons in the field (so that we now consider *continuum resonance* Raman scattering[2]). E is the energy label and η collects all other relevant quantum numbers. We may write

$$\langle e E\eta; \text{vac} | \mathcal{V} | i; k_0'', \lambda \rangle$$
$$= -i \sqrt{\frac{\hbar \omega_0''}{2\epsilon_0 L^3}} \langle e E\eta | d \cdot e_\lambda | i \rangle , \qquad (8)$$

$$\langle f; k_0', \mu | \mathcal{V} | e E\eta; \text{vac} \rangle = i \sqrt{\frac{\hbar \omega_0'}{2\epsilon_0 L^3}} \langle f | d \cdot e_\mu | e E\eta \rangle , \qquad (9)$$

so that the transition probability takes the form

$$P_{fi}(\overline{E}) = \frac{4\pi^2 \hbar^2 \omega_0'' \omega_0'}{(2\epsilon_0 L^3)^2}$$
$$\times \left| \lim_{\epsilon \to 0^+} \sum_{e\eta} \int dE \frac{\langle f | d \cdot e_\mu | e E\eta \rangle \langle e E\eta | d \cdot e_\lambda | i \rangle}{\overline{E} + i\epsilon - E} \right|^2 . \qquad (10)$$

Further progress is made by representing the molecular states with the zeroth order Born–Oppenheimer approximation. The various molecular wave functions can be written

$$\langle q, R, \alpha, \beta, \gamma | i \rangle = \varphi_g(q, R)$$
$$\times R^{-1} \chi_{n'' J'' \Omega''}(R) \psi_{J'' M'' \Omega''}(\alpha, \beta, \gamma) , \qquad (11a)$$

$$\langle q, R, \alpha, \beta, \gamma | e E\eta \rangle = \varphi_e(q, R)$$
$$\times R^{-1} \chi_{eEJ\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) , \qquad (11b)$$

$$\langle q, R, \alpha, \beta, \gamma | f \rangle = \varphi_g(q, R)$$
$$\times R^{-1} \chi_{n' J' \Omega'}(R) \psi_{J' M' \Omega'}(\alpha, \beta, \gamma) . \qquad (11c)$$

The electronic wave functions of the ground and excited states are $\varphi_g(q, R)$ and $\varphi_e(q, R)$ assumed to be real with q denoting collectively the electronic coordinates and R being the vector for the nuclear relative positions. The χ's are vibrational functions, the index E for $\chi_{eEJ\Omega}(R)$ indicating that in the excited state e we deal with a continuum. α, β, γ are the Euler angles defining the orientation of a molecular fixed reference frame in the laboratory frame. n is the vibrational quantum number, J the angular momentum quantum number, M and Ω its projections on the laboratory and molecular respective z axes. Introducing these functions into Eq. (10) gives

$$P_{fi}(\overline{E}) = \frac{4\pi^2 \hbar^2 \omega_0'' \omega_0'}{(2\epsilon_0 L^3)^2} \left| \lim_{\epsilon \to 0^+} \sum_{eJM\Omega} \int dE \frac{\langle gn' J' M' \Omega' | d \cdot e_\mu | eEJM\Omega \rangle_{q,R} \langle eEJM\Omega | d \cdot e_\lambda | gn'' J'' M'' \Omega'' \rangle_{q,R}}{\overline{E} - E + i\epsilon} \right|^2 . \qquad (12)$$

This transition probability can then be used to derive the differential cross section in the usual way.[9,10]

We have presented here this-by-now-standard derivation of the resonance Raman scattering probability to emphasize that this is providing only a formal solution. It remains to evaluate the various integrals making up (12). Integration over electronic coordinates and angles

presents no problem, but integration over the internuclear distance is not straightforward.

The reason for this treatment giving only a formal answer is that the description of the scattering of a photon requires the construction of entrance and exit channels with continua of photon states[11] with the molecule being involved only through the specification of its relevant states. Thus, these channels cannot serve to build into the theory the various molecular states, contrary to molecular collision theory,[12] where a system of coupled equations is formulated in such a way as to yield not only information on the collision itself but also on the properties of the partners. We are going to see that it is possible to formulate a set of coupled equations patterned after those of molecular collision theory which will have the property of providing directly (i.e., numerically) the information being sought. In order to qualify the differences between the two approaches, we may say that while in the treatment of Sec. II the molecule was the spectator, it is now the photons which will take up this role.

III. COUPLED CHANNEL EQUATIONS AND RAMAN SCATTERING

We try first of all a representation of the system molecule and field of the form

$$\Psi = \varphi_g(q, \mathbf{R}) R^{-1} U_{1gJ''M''\Omega''}(R) \psi_{J''M''\Omega''}(\alpha, \beta, \gamma) |\mathbf{k}_0'', \mathbf{e}_\lambda\rangle$$

$$+ \sum_{eJM\Omega} \varphi_e(q, \mathbf{R}) R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) |\text{vac}\rangle$$

$$+ \varphi_g(q, \mathbf{R}) R^{-1} U_{3gJ'M'\Omega'}(R) \psi_{J'M'\Omega'}(\alpha, \beta, \gamma) |\mathbf{k}_0', \mathbf{e}_\mu\rangle, \quad (13)$$

and take now for the total Hamiltonian

$$H = H_{BO} + H_F + \mathscr{V} = H_0 + \mathscr{V}, \quad (14)$$

where H_{BO} is an approximate molecular Hamiltonian having as exact eigenfunctions the Born–Oppenheimer products listed in Eq. (11). We observe that this corresponds to a mixture of molecular dressed states[13] such as those that are widely used in the description of molecular radiative collisions.[14] The unknown functions to be determined from the wave equation are the U_i's which have been indexed by reference to the corresponding rotational functions. Since (13) is a multicomponent representation, introduction of Ψ into

$$H\Psi = \bar{E}\Psi, \quad (15)$$

premultiplication by all known functions, and integration over the corresponding variables will produce a system of coupled equations for the U_i's. We start with eliminating the field variables, premultiplying by $\langle \mathbf{k}_0'', \mathbf{e}_\lambda |$, $\langle \text{vac} |$, or $\langle \mathbf{k}_0', \mathbf{e}_\mu |$, respectively. Because of the form taken for $\mathscr{V}$ [Eq. (7)], we obtain

$$(H_{BO} + \hbar\omega_0'' - \bar{E})\varphi_g(q, \mathbf{R}) R^{-1} U_{1gJ''M''\Omega''}(R) \psi_{J''M''\Omega''}(\alpha, \beta, \gamma) + i \sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}} \sum_{eJM\Omega} (\mathbf{d} \cdot \mathbf{e}_\lambda)\varphi_e(q, \mathbf{R}) R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) = 0,$$

$$(16a)$$

$$(H_{BO} - \bar{E})\varphi_e(q, \mathbf{R}) R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) - i \sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}} (\mathbf{d} \cdot \mathbf{e}_\lambda)\varphi_g(q, \mathbf{R}) R^{-1} U_{1gJ''M''\Omega''}(R) \psi_{J''M''\Omega''}(\alpha, \beta, \gamma)$$

$$- i \sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}} (\mathbf{d} \cdot \mathbf{e}_\mu)\varphi_g(q, \mathbf{R}) R^{-1} U_{3gJ'M'\Omega'}(R) \psi_{J'M'\Omega'}(\alpha, \beta, \gamma) = 0, \quad (16b)$$

$$(H_{BO} + \hbar\omega_0' - \bar{E})\varphi_g(q, \mathbf{R}) R^{-1} U_{3gJ'M'\Omega'}(R) \psi_{J'M'\Omega'}(\alpha, \beta, \gamma) + i \sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}} \sum_{eJM\Omega} (\mathbf{d} \cdot \mathbf{e}_\mu)\varphi_e(q, \mathbf{R}) R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) = 0. \quad (16c)$$

The next stage is the premultiplication of Eqs. (16a) and (16c) by $\varphi_g(q, \mathbf{R})$ and of Eq. (16b) by $\varphi_e(q, \mathbf{R})$ followed by integration over the electronic variables. This leads to the system

$$[\mathbf{T}_N + V_g(R) + \hbar\omega_0'' - \bar{E}] R^{-1} U_{1gJ''M''\Omega''}(R) \psi_{J''M''\Omega''}(\alpha, \beta, \gamma) + i \sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}} \sum_{eJM\Omega} (\mathbf{d}^e \cdot \mathbf{e}_\lambda) R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) = 0, \quad (17a)$$

$$[\mathbf{T}_N + V_e(R) - \bar{E}] R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) - i \sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}} (\mathbf{d}^e \cdot \mathbf{e}_\lambda) R^{-1} U_{1gJ''M''\Omega''}(R) \psi_{J''M''\Omega''}(\alpha, \beta, \gamma)$$

$$- i \sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}} (\mathbf{d}^e \cdot \mathbf{e}_\mu) R^{-1} U_{3gJ'M'\Omega'}(R) \psi_{J'M'\Omega'}(\alpha, \beta, \gamma) = 0, \quad (17b)$$

$$[\mathbf{T}_N + V_g(R) + \hbar\omega_0' - \bar{E}] R^{-1} U_{3gJ'M'\Omega'}(R) \psi_{J'M'\Omega'}(\alpha, \beta, \gamma) + i \sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}} \sum_{eJM\Omega} (\mathbf{d}^e \cdot \mathbf{e}_\mu) R^{-1} U_{2eJM\Omega}(R) \psi_{JM\Omega}(\alpha, \beta, \gamma) = 0. \quad (17c)$$

In Eqs. (17), $\mathbf{d}^e$ is the electronic transition moment

$$\mathbf{d}^e = \langle \varphi_g | \mathbf{d} | \varphi_e \rangle_q \quad (18)$$

assumed to be real, and $\mathbf{T}_N$ the internal nuclear kinetic energy operator. The final step is the premultiplication of Eq. (17a) by $\psi_{J''M''\Omega''}^*(\alpha, \beta, \gamma)$, of Eq. (17b) by $\psi_{JM\Omega}^*(\alpha, \beta, \gamma)$ and of Eq. (17c) by $\psi_{J'M'\Omega'}^*(\alpha, \beta, \gamma)$ followed by integration over angles. We obtain in this way

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_g(R) + \frac{\hbar^2[J''(J''+1) - \Omega''^2]}{2\mu R^2} + \hbar\omega_0'' - \bar{E} \right] U_{1gJ''M''\Omega''}(R) + i \sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}} \sum_{eJM\Omega} \langle J''M''\Omega'' | \mathbf{d}^e \cdot \mathbf{e}_\lambda | JM\Omega \rangle U_{2eJM\Omega}(R) = 0$$

$$(19a)$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_e(R) + \frac{\hbar^2[J(J+1)-\Omega^2]}{2\mu R^2} - \overline{E}\right] U_{2eJM\Omega}(R) - i\sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}}\langle JM\Omega|\mathbf{d}^e\cdot\mathbf{e}_\lambda|J''M''\Omega''\rangle U_{1gJ''M''\Omega''}(R)$$

$$-i\sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}}\langle JM\Omega|\mathbf{d}^e\cdot\mathbf{e}_\mu|J'M'\Omega'\rangle U_{3gJ'M'\Omega'}(R) = 0 ,\qquad (19b)$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_g(R) + \frac{\hbar^2[J'(J'+1)-\Omega'^2]}{2\mu R^2} + \hbar\omega_0' - \overline{E}\right]$$

$$\times U_{3gJ'M'\Omega'}(R) + i\sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}}\sum_{eJM\Omega}\langle J'M'\Omega'|\mathbf{d}^e\cdot\mathbf{e}_\mu|JM\Omega\rangle U_{2eJM\Omega}(R) = 0 .\qquad (19c)$$

μ is the reduced mass of the diatomic. We observe that this system of equations has the following properties:

(a) If the coupling between the molecule and the field is ignored, the equations are decoupled and the U_i's are nothing but the vibrational functions χ_i's which are used in building the Born–Oppenheimer products (11). These functions do not depend on M, but we will maintain the indexing introduced in Eq. (13). The eigenkets of the decoupled equations are therefore noted $|1gn''J''M''\Omega''\rangle$, $|2eEJM\Omega\rangle$, $|3gn'J'M'\Omega'\rangle$, but to avoid confusion with rovibronic states, matrix elements built with these states will bear a subscript R.

(b) The eigenenergies of the decoupled equations (19a) and (19c) are the bound molecular energies pushed upwards by $\hbar\omega_0''$ or $\hbar\omega_0'$. Thus, these equations produce the energies of the dressed molecule. On the other hand, the potential in Eq. (19b) is that of the naked molecule. This means that we may in general expect curve crossings between the molecular potentials. This is illustrated in Fig. 1. Figure 1(a) shows the molecular potentials of two electronic states g and e with some of their energy levels. Figure 1(b) takes into account the energies of the incoming and outgoing photons. The ground state molecular potential is represented twice (because the field offers additional degrees of freedom, these are independent channels for the composite system).

(c) The first and last channels are closed at energy $\overline{E}$. Each of the open channels corresponding to one of the equations (19b) is only coupled to the two closed channels. It would be quite possible to solve the system of Eqs. (19) using any of the available algorithms for the treatment of multichannel equations. However the S matrix obtained in this way would reflect the coupling between open channels via the closed ones. The physics of the Raman scattering, on the contrary, reflects the coupling of the closed channels (initial and final) via the open ones. We are therefore going to extend somewhat this system of coupled equations so that the new S matrix may be used to derive the resonance Raman scattering amplitudes. This is done by introducing two additional artificial open channels in such a way that the bound levels of the closed channels act as doorway states between continua. This type of extension of the multichannel equations was proposed first by Shapiro[6] and can be used in the study of predissociation and photodissociation which involve bound states coupled to continua.[15,16] We assume for the two additional channel equations the form

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_a(R) - \overline{E}\right] U_a(R) + \beta U_{1gJ''M''\Omega''}(R) = 0 ,\qquad (20a)$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_b(R) - \overline{E}\right] U_b(R) + \beta U_{3gJ'M'\Omega'}(R) = 0 .\qquad (20b)$$

The potentials $V_a(R)$ and $V_b(R)$ can be chosen somewhat arbitrarily but must guarantee some coupling between channels a and 1 on one hand and 3 and b on the other. β is a constant to be chosen according to a criterion to be given below. Equations (20a) and (20b) with $\beta=0$ have eigenkets denoted $|a\overline{E}\rangle$ and $|b\overline{E}\rangle$. We introduce also at this point a dimensionless scaling factor β_0 in all interchannel couplings in Eqs. (19).

We assume now that states $|1gn''J''M''\Omega''\rangle$ and $|3gn'J'M'\Omega'\rangle$ are sufficiently well separated from the other bound states of their respective channels (in the sense that the widths the various bound levels gain by being coupled to continua are much smaller than the level separations), so that at an energy $\overline{E}$ such that $\overline{E} \sim E_i + \hbar\omega_0'' = E_f + \hbar\omega_0'$ scattering from channel a to channel b is possible only through those states. The factor β and the scaling factor β_0 can always be chosen sufficiently small so as to ensure such a situation. The element $S_{ba}(\overline{E})$ of the S matrix can be derived under this assumption. The uncoupled equations for the open channels admit as solutions functions which go asymptotically as $\sin[k_i R + \eta_i(\overline{E})]$ $(i = a, eJM\Omega, b)$. These are the
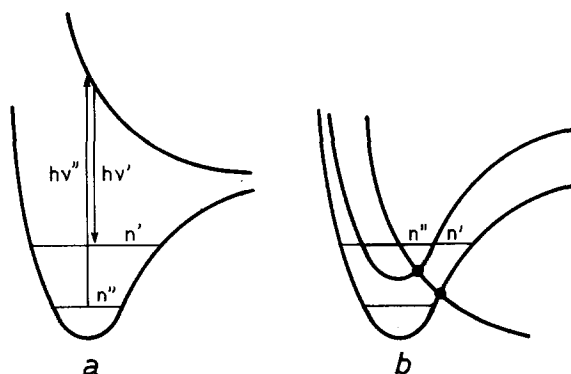

FIG. 1. Molecular potentials involved in $n' \leftarrow n''$ Raman scattering via a continuum of excited states: (a) without consideration of the photon energies; (b) for the dressed molecule. Dots indicate the radiative crossings which are associated with the transitions.

distorted waves which take into account the elastic part of the interaction. The S matrix is obtained by an analysis of the asymptotic channel functions in terms of free waves. We have the relation[12]

$$S_{ba}(\overline{E}) = e^{i\,\eta_b\,(\overline{E})}S_{ba}^D(\overline{E})\,e^{i\,\eta_a\,(\overline{E})}\ , \tag{21}$$

where $S_{ba}^D(\overline{E})$ corresponds to an asymptotic analysis in terms of distorted waves. This element $S_{ba}^D(\overline{E})$ can be obtained from [cf. Eqs. (4) and (6)]

$$S_{ba}^D(\overline{E}) = -2i\pi\langle b\overline{E}|\mathbf{V}|3gn'J'M'\Omega'\rangle_R$$

$$\times \langle 3gn'J'M'\Omega'|\mathbf{G}^+(\overline{E})|1gn''J''M''\Omega''\rangle_R$$

$$\times \langle 1gn''J''M''\Omega''|\mathbf{V}|a\overline{E}\rangle_R\ . \tag{22}$$

The matrix element $\langle 3gn'J'M'\Omega'|\mathbf{G}(z)|1gn''J''M''\Omega''\rangle_R$ of the Green function is derived in the Appendix. It has the form

$$\langle\rho|\mathbf{G}(z)|\sigma\rangle_R = \frac{\mathfrak{R}_{\rho\sigma}(z)}{[z - E_\rho - \hbar\omega_0' - \mathfrak{R}_{\rho\rho}(z)][z - E_\sigma - \hbar\omega_0'' - \mathfrak{R}_{\sigma\sigma}(z)] - \mathfrak{R}_{\rho\sigma}(z)\mathfrak{R}_{\sigma\rho}(z)}\ , \tag{23}$$

where ρ stands for $3gn'J'M'\Omega'$ and σ for $1gn''J''M''\Omega''$. The operator $\mathfrak{R}$ is

$$\mathfrak{R}(z) = \mathbf{V}\mathbf{Q}[z - \mathbf{Q}\mathbf{H}_0\mathbf{Q}]^{-1}\mathbf{Q}\mathbf{V}\ , \tag{24}$$

where $\mathbf{Q}$ is the projection operator onto the subspace of solutions for the uncoupled channels a, $eJM\Omega$ and b and $\mathbf{V}$ the interchannel coupling. An element such as $\mathfrak{R}_{\rho\rho}(z)$ in the denominator of Eq. (23) is producing

$$\lim_{\epsilon\to0^+}\mathfrak{R}_{\rho\rho}(z) = \Delta_\rho(\overline{E}) - i\Gamma_\rho(\overline{E})\ , \tag{25}$$

with

$$\Delta_\rho(\overline{E}) = \mathscr{P}\int dE$$

$$\times \frac{|\langle bE|\mathbf{V}|3gn'J'M'\Omega'\rangle_R|^2 + \sum_{eJM\Omega}|\langle 3gn'J'M'\Omega'|\mathbf{V}|2eEJM\Omega\rangle_R|^2}{\overline{E} - E}\ , \tag{26}$$

and

$$\Gamma_\rho(\overline{E}) = \pi\left\{|\langle b\overline{E}|\mathbf{V}|3gn'J'M'\Omega'\rangle_R|^2 + \sum_{eJM\Omega}|\langle 3gn'J'M'\Omega'|\mathbf{V}|2e\overline{E}JM\Omega\rangle_R|^2\right\}\ . \tag{27}$$

These quantities are analogous to a level shift and a level width,[17] but this would be so only if we had $\overline{E} = E_{n'J'M'\Omega'} + \hbar\omega_0'$. The matrix elements present in Eqs. (26) and (27) can be written

$$\langle bE|\mathbf{V}|3gn'J'M'\Omega'\rangle_R = \beta\langle bE|3gn'J'M'\Omega'\rangle_R\ , \tag{28}$$

$$\langle 3gn'J'M'\Omega'|\mathbf{V}|2eEJM\Omega\rangle_R = i\sqrt{\frac{\hbar\omega_0'}{2\epsilon_0 L^3}}\beta_0\langle gn'J'M'\Omega'|\mathbf{d}\cdot\mathbf{e}_\mu|eEJM\Omega\rangle_{q,R}\ . \tag{29}$$

A similar decomposition can be made for $\lim_{\epsilon\to0^+}\mathfrak{R}_{\sigma\sigma}(z)$ which will contain the matrix elements

$$\langle 1gn''J''M''\Omega''|\mathbf{V}|aE\rangle_R = \beta\langle 1gn''J''M''\Omega''|aE\rangle_R\ , \tag{30}$$

$$\langle 2eEJM\Omega|\mathbf{V}|3gn''J''M''\Omega''\rangle_R = -i\sqrt{\frac{\hbar\omega_0''}{2\epsilon_0 L^3}}\beta_0\langle eEJM\Omega|\mathbf{d}\cdot\mathbf{e}_\lambda|gn''J''M''\Omega''\rangle_{q,R}\ . \tag{31}$$

It must be realized in examining the matrix element given by Eq. (29) [or (31)] that $\mathbf{V}$ between channels 3 and $eJM\Omega$ (or between channels $eJM\Omega$ and 1) is nothing but the off-diagonal element of the potential matrix in Eq. (19c) [or Eq. (19a)]. Since this element implies already integration over electronic coordinates and angles, the matrix element in Eq. (29) [or (31)] is involving integration over all coordinates of the molecular states. The elements in Eqs. (28) and (30) are the same that came out as factors in Eq. (22). Finally, there is the relation

$$\mathfrak{R}_{\rho\sigma}(z) = \frac{\hbar^2(\omega_0''\omega_0')^{1/2}}{2\epsilon_0 L^3}\beta_0^2\sum_{eJM\Omega}\int dE\,\frac{\langle gn'J'M'\Omega'|\mathbf{d}\cdot\mathbf{e}_\mu|eEJM\Omega\rangle_{qR}\langle eEJM\Omega|\mathbf{d}\cdot\mathbf{e}_\lambda|gn''J''M''\Omega''\rangle_{qR}}{\overline{E} + i\epsilon - E}\ . \tag{32}$$

Apart from a factor, this is just the transition amplitude given by Eq. (12) and needed for the calculation of the transition probability for resonance Raman scattering.

We see by comparison of Eqs. (21), (22), (23), (26), and (27) that knowledge of $S_{ba}(\overline{E})$, $\eta_a(\overline{E})$, $\eta_b(\overline{E})$, $\langle b\overline{E}|\mathbf{V}|3gn'J'M'\Omega'\rangle_R$, $\langle 1gn''J''M''\Omega''|\mathbf{V}|a\overline{E}\rangle_R$, $\Delta_{3gn'J'M'\Omega'}$, $\Gamma_{3gn'J'M'\Omega'}$, $\Delta_{1gn''J''M''\Omega''}$, and $\Gamma_{1gn''J''M''\Omega''}$

leads to a knowledge of the resonance Raman scattering amplitude. The element $S_{ba}(\overline{E})$ is the output of a multichannel calculation. The phases $\eta_a(\overline{E})$ and $\eta_b(\overline{E})$ can be obtained in various ways: one channel calculations or analytical expressions valid for some simple potentials (the potentials of channels a and b being somewhat arbitrary). The couplings can be obtained from two-channel calculations. The Δ's and Γ's can also be obtained from

two-channel calculations by analyzing the phase shift in the open channel for two potentials placed in such a way that the resonances fall at energy $\bar{E}$. The bound state energies $E_{n''J''M''\Omega''}$ and $E_{n'J'M'\Omega'}$ can sometimes be obtained analytically, but numerical procedures are also available. The Raman scattering amplitude is then obtained as a complex root of a second order polynomial [cf. Eq. (23), showing that the square of the amplitude is present in the denominator of the relevant element of the Green function].

We now make the following remarks on this procedure for estimating the resonance Raman scattering amplitudes.

Although the starting point is a multicomponent function [Eq. (13)] which could show how the vibrational factors U_i could be made different from the corresponding χ_i of the Born–Oppenheimer product functions by the molecule–field interaction, the purpose of the present formalism is not an investigation of such an effect. Quite to the contrary, thanks to appropriate scaling factors, the couplings should be made sufficiently small so to ensure that the distorted wave solution given to the problem is closed to the numerical solution. This is because all we need for estimating the scattering amplitude are the vibrational functions of the BO representation. This represents a somewhat paradoxical situation: in usual scattering problems the Born distorted wave

transition amplitudes are estimated when the exact coupled channel equations are considered to be too difficult to solve. In our situation, the amplitude we are looking for can be written as the Born distorted wave transition amplitude of some close coupling problem. Because the solution of this problem is, numerically speaking, not too difficult to obtain, we use this solution to estimate our transition amplitude.

It remains, of course, to prove that the procedure is producing the scattering amplitudes with sufficient accuracy. This can be done if we dispose, at least for some particular cases, of a different and accurate method. The harmonic–linear case is providing such a test, since it can be treated analytically (Sec. IV).

Equation (32) shows that $\mathfrak{R}_{\rho o}(z)$ is a sum of terms, one for each continuum of excited states labeled $eJM\Omega$. Thus, instead of solving the system of equations (19) and (20) we could consider five coupled equations with the two artificial channels, the two closed channels defining the initial and final bound states and the channel indexed by $eJM\Omega$. Such a calculation would have to be repeated for each term contributing to Eq. (32). We show in the next section that such systems of coupled equations still contain some superfluous information and that it is possible to obtain the scattering amplitudes from an even simpler set of coupled equations.

IV. REDUCED COUPLED CHANNEL EQUATIONS

We start again from the amplitude

$$\mathcal{A}_{n'J'M',n''J''M''}^{\mu\lambda}(\bar{E}) = \lim_{\epsilon\to 0^+} \sum_{eJM\Omega} \int dE \, \frac{\langle gn'J'M'0|\mathbf{d}\cdot\mathbf{e}_\mu|eEJM\Omega\rangle_{q,\mathbf{R}}\langle eEJM\Omega|\mathbf{d}\cdot\mathbf{e}_\lambda|gn''J''M''0\rangle_{q,\mathbf{R}}}{\bar{E}-E+i\epsilon} , \tag{33}$$

where we now consider that in both initial and final states $\Omega = 0$, this being the case for the practical applications to be considered later. The purpose of the transformation to be made here is to disentangle the effect of the electronic and rotational parts of the wave function from that part linked to vibration since it is only the latter which requires really our attention. The electronic functions are in fact only providing the electronic transition moment, and the integration over angles can be performed by using the known properties of the rotational functions. Although no basic information is being lost by this simplified scheme, this avoids the evaluation of a coupling matrix depending on rotational functions in the formulation of the coupled equations [cf. Eq. (19)]. All rotational properties can be restored at a later stage [cf. Eqs. (39) and (40) below].

The polarization vectors $\mathbf{e}_\lambda, \mathbf{e}_\mu$ could be any pair chosen among e_x, e_y, and e_z, where x, y, z are the axis of a laboratory frame. In order to take full advantage of the properties of rotational functions, it is preferable to consider them to be any pair taken among the combinations

$$|e_0'\rangle = |e_z\rangle ; \quad |e_\pm\rangle = \mp \frac{1}{\sqrt{2}}\{|e_x\rangle \pm i|e_y\rangle\} , \tag{34}$$

and to build in a similar way combinations of the components of $\mathbf{d}$ which behave as an irreducible tensor of order 1:

$$d_0 = d_z ; \quad d_\pm = \mp \frac{1}{\sqrt{2}}\{d_x \pm id_y\} . \tag{35}$$

The rotational functions can be written[18]

$$\psi_{JM\Omega}(\alpha,\beta,\gamma) = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} R_{M\Omega}^{J*}(\alpha,\beta,\gamma) , \tag{36}$$

$R_{M\Omega}^{J*}$ being an element of the rotation matrix R^{J*}. In Eq. (33), integration over the electronic coordinates can be performed first. This leads to the components of the electronic transition moment in the space fixed axis

$$d_\lambda^e(R,\alpha,\beta,\gamma) = \langle e|d_\lambda|g\rangle_q , \tag{37}$$

which can be related to the components in the body fixed frame according to

$$d^e_\chi(R, \alpha, \beta, \gamma) = \sum_\zeta R^1_{\lambda\zeta}(\alpha, \beta, \gamma) D^e_\zeta(R) \ . \tag{38}$$

It is then possible to integrate out over angle variables and to obtain[19]

$$\mathscr{A}^{\mu\lambda}_{n'J'M', n''J''M''}(\overline{E}) = \left(\frac{2J''+1}{2J'+1}\right)^{1/2} \sum_{JM\Omega} \sum_{\zeta\xi} \langle J''1M''\mu | JM\rangle \langle J1M\lambda | J'M'\rangle \langle J''10\zeta | J\Omega\rangle \langle J1\Omega\xi | J'0\rangle \alpha^{\zeta\xi}_{n'J', J\Omega, n''J''}(\overline{E}) \ , \tag{39}$$

with

$$\alpha^{\zeta\xi}_{n'J', J\Omega, n''J''}(\overline{E}) = \lim_{\epsilon\to 0^+} \sum_e \int dE \ \frac{\langle n'J' | D^e_\zeta | eEJ\Omega\rangle_R \langle eEJ\Omega | D^e_\xi | n''J''\rangle_R}{\overline{E} - E + i\epsilon} \ . \tag{40}$$

$\langle J''1M''\mu | JM\rangle$, etc. are the usual Clebsch–Gordan coefficients. We use at this point the fact that will be demonstrated in Paper II—that taking J different from J'' or J' has only little effect on the amplitudes given by Eq. (40). Since Ω which affects the centrifugal energy [cf. Eqs. (19)] can only take the values 0, ±1, we may safely also ignore its effect on $\alpha^{\zeta\xi}_{n'J', J\Omega, n''J''}(\overline{E})$ which can be noted $\overline{\alpha}^{\zeta\xi}_{n'J', n''J''}(\overline{E})$ with the definition

$$\overline{\alpha}^{\zeta\xi}_{n'J', n''J''}(\overline{E}) = \lim_{\epsilon\to 0^+} \sum_e \int dE \ \frac{\langle n'J' | D^e_\zeta | eEJ''\rangle_R \langle eEJ'' | D^e_\xi | n''J''\rangle_R}{\overline{E} - E + i\epsilon} \ , \tag{41}$$

where the kets (or bra) are all of vibrational type. Considerable simplifications result in Eq. (39) from this assumption. Thus we find

$$\mathscr{A}^{\mu\lambda}_{n'J'M', n''J''M''}(\overline{E}) = \left(\frac{2J''+1}{2J'+1}\right)^{1/2} \sum_{j=0}^{2} C_j(\overline{E}) \langle J''jM''\mu+\lambda | J'M'\rangle \langle 11\lambda\mu | j\mu+\lambda\rangle \langle J''j00 | J'0\rangle \ , \tag{42}$$

with

$$C_j(\overline{E}) = \sum_{\zeta\xi} \langle 11\xi\zeta | j0\rangle \overline{\alpha}^{\zeta\xi}_{n'J', n''J''}(\overline{E}) \ . \tag{43}$$

In order to calculate any of the amplitudes found in Eq. (41), let us consider the system of five coupled equations:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_a(R) - \overline{E}\right] U_a(R) + \beta U_{1J''}(R) = 0 \ , \tag{44a}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_\ell(R) + \frac{\hbar^2 J''(J''+1)}{2\mu R^2} + \hbar\omega''_0 - \overline{E}\right] U_{1J''}(R) + \beta\left(U_a(R) + \frac{D^e_\zeta(R)}{D^e_\zeta(R_0)} U_{2eJ''}(R)\right) = 0 \ , \tag{44b}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_e(R) + \frac{\hbar^2 J''(J''+1)}{2\mu R^2} - \overline{E}\right] U_{2eJ''}(R) + \beta\left(\frac{D^e_\zeta(R)}{D^e_\zeta(R_0)} U_{1J''}(R) + \frac{D^e_\xi(R)}{D^e_\xi(R_0)} U_{3J'}(R)\right) = 0 \ , \tag{44c}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_\ell(R) + \frac{\hbar^2 J'(J'+1)}{2\mu R^2} + \hbar\omega'_0 - \overline{E}\right] U_{3J'}(R) + \beta\left(\frac{D^e_\xi(R)}{D^e_\xi(R_0)} U_{2eJ''}(R) + U_b(R)\right) = 0 \ , \tag{44d}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V_b(R) - \overline{E}\right] U_b(R) + \beta U_{3J'}(R) = 0 \ . \tag{44e}$$

In agreement with our previous discussion, we take the same centrifugal energies for both initial ground state and excited state. In these equations, R_0 is some reference point, for instance the equilibrium distance of the ground state. The analysis given previously for the system [Eq. (19)] is still valid. The bound states of channels 1 and 3 may still act as doorway states between a and 2 on one hand, 2 and b on the other. The eigenstates of the decoupled equations are now noted $| a\overline{E}\rangle$, $| n''J''\rangle$, $| eEJ''\rangle$, $| n'J'\rangle$, and $| b\overline{E}\rangle$. All matrix elements are implying integration only over R, so that no subscript is needed.

The basic formulas are now, together with [Eq. (21)],

$$S^D_{ba}(\overline{E}) = -2i\pi\langle b\overline{E} | \mathbf{V} | n'J'\rangle \langle n'J' | \mathbf{G}^+(\overline{E}) | n''J''\rangle \langle n''J'' | \mathbf{V} | a\overline{E}\rangle \ , \tag{45}$$

and

$$\langle n'J' | \mathbf{G}(z) | n''J''\rangle = \frac{\mathcal{R}^e_{n'J', n''J''}(z)}{[z - E_{n'J'} - \hbar\omega'_0 - \mathcal{R}^e_{n'J', n'J'}(z)][z - E_{n''J''} - \hbar\omega''_0 - \mathcal{R}^e_{n''J'', n''J''}(z)] - \mathcal{R}^e_{n'J', n''J''}(z)\mathcal{R}^e_{n''J'', n'J'}(z)} \ . \tag{46}$$

The quantities such as Eqs. (26) and (27) take the simpler form

$$\Delta_{n'J'}(\overline{E}) = \int dE \ \frac{| \langle bE | \mathbf{V} | n'J'\rangle |^2 + | \langle n'J' | \mathbf{V} | eEJ''\rangle |^2}{\overline{E} - E} \ , \tag{47}$$

$$\Gamma_{n'J'}(\overline{E}) = \pi[| \langle b\overline{E} | \mathbf{V} | n'J'\rangle |^2 + | \langle n'J' | \mathbf{V} | e\overline{E}J''\rangle |^2] \ . \tag{48}$$

The matrix elements in Eqs. (47) and (48) are now

$$\langle bE|\mathbf{V}|n'J'\rangle = \beta\,\langle bE|n'J'\rangle ,\tag{49}$$

$$\langle n'J'|\mathbf{V}|eEJ''\rangle = \frac{\beta}{D^e_\zeta(R_0)}\langle n'J'|D^e_\zeta|eEJ''\rangle .\tag{50}$$

Finally,

$$\mathfrak{R}^e_{n'J',n''J''}(\overline{E}) = \frac{\beta^2}{D^e_\zeta(R_0)D^e_\zeta(R_0)}\lim_{\epsilon\to 0^+}\int dE\,\frac{\langle n'J'|D^e_\zeta|eEJ''\rangle_R\langle eEJ''|D^e_\zeta|n''J''\rangle_R}{\overline{E}-E+i\epsilon} .\tag{51}$$

Thus we have

$$\beta^{-2}\sum_e D^e_\zeta(R_0)D^e_\zeta(R_0)\mathfrak{R}^e_{n'J',n''J''}(\overline{E}) = \overline{\alpha}^{\zeta\zeta}_{n'J',n''J''}(\overline{E}) ,\tag{52}$$

and the element $S_{ba}(\overline{E})$ of the **S** matrix corresponding to the systems [Eq. (44)] may serve to reach the quantities $\overline{\alpha}^{\zeta\zeta}_{n'J',n''J''}(\overline{E})$ which in turn will lead to the scattering amplitude through [Eq. (42)].

It is useful at this point to recall that coupled equations are used here simply as a means to obtain in a convenient way an estimate for an expression which represents the distorted wave Born approximation of the multichannel system. There is a way, as shown by Shapiro,[6] to modify the potential matrix in order to make this correspondence even closer. This is by introducing a non-Hermitian coupling matrix. Returning to the system of Eqs. (44), we now assume channel a to be coupled to 1, channel 1 to be coupled to 2, and so on, in a chainlike manner. This means using a potential matrix which has off-diagonal elements on one side only of the diagonal. In this case, as shown in the Appendix, the consequences are

$$\mathfrak{R}^e_{n''J'',n'J'}(z) = \mathfrak{R}^e_{n'J',n'J'}(z) = \mathfrak{R}^e_{n''J'',n''J''}(z) = 0 .\tag{53}$$

Thus, Eqs. (46) reduces to

$$\langle n'J'|\mathbf{G}(z)|n''J''\rangle = \frac{\mathfrak{R}^e_{n'J',n''J''}(z)}{(z-E_{n'J'}-\hbar\omega'_0)(z-E_{n''J''}-\hbar\omega''_0)} ,\tag{54}$$

and extraction of $\mathfrak{R}^e_{n'J',n''J''}(\overline{E})$ requires only the solution of a first order equation. In addition the phases $\eta_a(\overline{E})$ and $\eta_b(\overline{E})$ can be obtained directly from $S_{aa}(\overline{E})$ and $S_{bb}(\overline{E})$ (cf. Appendix). With regard to possible corrections to $S_{ba}(\overline{E})$ due to the existence of more than one discrete state between continua, we note the superiority of this asymmetrical scheme. Because the scattering matrix has real poles, decreasing $(\overline{E}-E_{n'J'}-\hbar\omega'_0)$, which amounts to decreasing also $(\overline{E}-E_{n''J''}-\hbar\omega''_0)$, has the effect that the term which has been selected in $S_{ba}(\overline{E})$ can be made in principle as dominant as one wishes. However this requires the differences $(\overline{E}-E_{n'J'}-\hbar\omega'_0)$ and $(\overline{E}-E_{n''J''}-\hbar\omega''_0)$ to be accurately known. This can be done by searching for the collision energy $\overline{E}$ which maximizes the transition probability. A discussion of this point will be made in Sec. V.

We consider now the problem of obtaining $\overline{\alpha}^{\zeta\zeta}_{n'J',n''J''}(\overline{E})$ as a function of $\overline{E}$, this amounting to a study of the scattering as a function of the frequency of the incoming photon. Although there is an $\overline{E}$ dependence in the expression derived for $\overline{\alpha}^{\zeta\zeta}_{n'J',n''J''}(\overline{E})$, varying $\overline{E}$ in the coupled equations over a wide range would imply that $|n''J''\rangle$ and $|n'J'\rangle$ are very quickly no longer doorway states in the scattering. A different procedure consists in shifting the potential in channel 2, which corresponds to the excited molecular electronic state. In the case of an asymmetrical coupling matrix, this is very convenient since auxiliary quantities such as phases and couplings remain the same all throughout the calculation of an excitation profile corresponding to given quantum numbers for initial and final states.

Finally, we mention another possibility which could be exploited.[20] This consists in using four channels, with channels 1 and 3 open and corresponding to the excited state, and channels 2 and 4 identical to channels 1 and 3 used in the present formulation. In the assumption of a cyclic and asymmetrical coupling matrix there is the following formula for, say, element $S_{aa}(\overline{E})$ of the scattering matrix

$$S_{aa}(\overline{E}) = -2i\pi\,e^{2i\eta_a(\overline{E})}\langle a\overline{E}|\mathbf{V}|n'J'\rangle\langle n'J'|\mathbf{G}^+(\overline{E})|n''J''\rangle\langle n''J''|\mathbf{V}|a\overline{E}\rangle .\tag{55}$$

The matrix element of G involved in Eq. (55) is (cf. Appendix)

$$\langle n'J'|\mathbf{G}^+(\overline{E})|n''J''\rangle = \frac{\mathfrak{R}^e_{n'J',n''J''}(\overline{E})}{(\overline{E}-E_{n'J'}-\hbar\omega'_0)(\overline{E}-E_{n''J''}-\hbar\omega''_0)-\mathfrak{R}^e_{n'J',n''J''}(\overline{E})\mathfrak{R}^e_{n''J'',n'J'}(\overline{E})} .\tag{56}$$

By cyclic and asymmetrical, we mean that channel 1 is coupled to 2, 2 to 3, 3 to 4, and finally, 4 to 1. However, in this procedure changing $\overline{E}$ requires evaluating $\langle 1\overline{E}|\mathbf{V}|n'J'\rangle$ and $\langle n''J''|\mathbf{V}|1\overline{E}\rangle$ for the new photon energy.

In the next section numerical tests are performed by comparison with the results of an analytically soluble case. We have previously[5] made a comparison of results obtained with either a symmetrical or an asymmetrical coupling matrix and have shown that the results are of comparable accuracy. All calculations to be presented now and in the next paper are done with the asymmetrical scheme, which has several advantages over the symmetrical one. The algorithm[21] used to solve the multichannel equations is based on the Fox method.[22] In this work, as well as in several other studies, we have found it to be accurate and reasonably fast.

V. RESONANCE RAMAN SCATTERING FOR HARMONIC AND LINEAR POTENTIALS: COMPARISON OF COUPLED CHANNEL RESULTS WITH EXACT AND SEMICLASSICAL ESTIMATES

We have already given in a previous publication[5] the formula that represents the exact Raman scattering amplitude when the initial and final states correspond to two discrete states of the same harmonic potential, while the potential of the excited states is linear. This exact formulation is important in the present context since it gives a mean of assessing the numerical accuracy of the coupled channel procedure. It could also, in principle, be used to calculate resonance Raman spectra since an harmonic representation for the lowest vibrational states of the electronic ground state and a linear representation for an excited state are not completely unrealistic. However, there are some numerical problems connected with this analytical formula, which will be discussed at the end of this section. We describe now the main features of this expression and indicate the computational steps, not given in Ref. 5.

Four parameters only are involved: the reduced mass of the diatomic μ, the angular frequency in the lower electronic state ω, the slope of the higher potential F, and the turning point in the excited state at the incoming photon energy $R_T(\overline{E})$. Our derivation follows that given by Sink and Bandrauk[23,24] for the calculation of level widths and shifts for these same potentials. Use is made of the momentum representations of the nth state of the harmonic potential and of the continuum states of the linear potential

$$\langle p \mid n \rangle = i^n/(2^n n!)^{1/2}(\pi\mu\omega\hbar)^{-1/4}\exp(-p^2/2\mu\omega\hbar)H_n[-p(\mu\omega\hbar)^{-1/2}] , \tag{57}$$

$$\langle p \mid E \rangle = (2\pi\hbar F)^{-1/2}\exp[i/\hbar F(p^3/6\mu - Ep)] , \tag{58}$$

where H_n is the nth Hermite polynomial. Using the formula

$$(\overline{E} - i\epsilon - E)^{-1} = -i\int_0^\infty [\exp it(\overline{E} + i\epsilon - E)]\,dt \tag{59}$$

leads for the scattering amplitudes to a quadruple integral. Integration over E produces a δ function. Integration over momenta is performed next. The remaining integral can be divided into two parts, one of which, according to Moyer's formulas,[25] is a combination of regular and irregular Airy functions, the other of which remains to be evaluated. If $I_{n'n''}(\overline{E})$ is a notation for

$$I_{n'n''}(\overline{E}) = \lim_{\epsilon\to 0^+}\int_{-\infty}^{+\infty}\frac{\langle n' \mid E\rangle\langle E \mid n''\rangle}{\overline{E} + i\epsilon - E}\,dE , \tag{60}$$

which is a special form of $\overline{\alpha}^{\xi\zeta}_{n'j',n''j''}(\overline{E})$ when there is no rotation and when $D_\xi = D_\zeta = 1$, there is finally the formula

$$I_{n'n''}(\overline{E}) = -\frac{\overline{\xi}}{(2^{n'}n'!)^{1/2}(2^{n''}n''!)^{1/2}}\sum_{k=0}^{n''}\sum_{l=0}^{n'}\binom{n''}{k}\binom{n'}{l}(8a)^{(k+l)/2}H_{n-k}(8a^3)H_{n'-l}(8a^3)$$

$$\times\{2\pi^{3/2}\,\mathrm{Ai}^{(k)}(z_0)[\mathrm{Bi}^{(l)}(z_0) - i\,\mathrm{Ai}^{(l)}(z_0)] + \partial^{k+l}\Phi(z, z')/\partial z^k\,\partial z'^{l}\big|_{r=s=0}\} . \tag{61}$$

The various symbols in Eq. (61) are the following functions of the basic parameters

$$a = \gamma^{2/3}/2\mu\hbar\omega , \tag{62a}$$

$$\gamma = 2\mu\hbar F , \tag{62b}$$

$$z = a^2 + q - 2i(2a\gamma)^{1/2} , \tag{63a}$$

$$q = \gamma^{1/3}R_T(\overline{E})/\hbar , \tag{63b}$$

$$z' = a^2 + q + 2i(2as)^{1/2} , \tag{64a}$$

$$z_0 = a^2 + q , \tag{64b}$$

$$\overline{\xi} = \frac{1}{\hbar F}\frac{\gamma^{2/3}}{(\mu\omega\hbar)^{1/2}}\exp(\tfrac{4}{3}a^3 + 2aq) . \tag{65}$$

In Eqs. (63a) and (64a), r and s are the parameters appearing in the generating forms of the Hermite polynomials such as

$$H_n(x) = \partial^n e^{-2rx}e^{-r^2}/\partial r^n\big|_{r=0} , \tag{66}$$

$\mathrm{Ai}^{(l)}$ and $\mathrm{Bi}^{(l)}$ are the lth derivatives of the regular and irregular Airy functions.[26] The main computational difficulties are connected with the evaluation of the last term of Eq. (61),

$$\partial^{k+l}\Phi(z, z')/\partial z^k\,\partial z'^{l}\big|_{r=s=0} , \tag{67}$$

where

$$\Phi(z, z') = \int_{2a}^0 du\,u^{-1/2}A(u) , \tag{68}$$

with

$$A(u) = \exp\left(\frac{u^3}{12} - \frac{(z + z')}{2}u - \frac{(z - z')^2}{4u}\right) . \tag{69}$$

Let us call $D(k, l)$ the operator $\partial^{k+l}/\partial z^k\,\partial z'^{l}$. A vertical bar to the right will indicate that all quantities in the equations have to be taken with $r = s = 0$. There are the two recurrence formulas

$$D(k, l)\Phi(z, z')\big| = z'D(k, l-2)\Phi(z, z')\big| - D(k, l-2)f(z, z')\big|$$
$$+ (l-2)D(k, l-3)\Phi(z, z')\big| , \tag{70}$$

$$D(k, l)\Phi(z, z')\big| = z\,D(k-2, l)\Phi(z, z')\big| - D(k-2, l)f(z, z')\big|$$
$$+ (k-2)D(k-3, l)\Phi(z, z')\big| . \tag{71}$$

In Eqs. (70) and (71), $f(z, z')$ is the quantity

$$f(z, z') = (2a)^{-1/2}\exp\left(2\frac{a^3}{3} - a(z + z') - \frac{(z - z')^2}{8a}\right) . \tag{72}$$

TABLE I. Comparisons of some results obtained for a harmonic–linear case (parameters in the text) with (a) the analytical formulation, (b) coupled equations, (c) a semiclassical formulation. Results in cm and cm², respectively.

| n' | n'' | $\Delta_{n'n''}$ | | | $\Gamma_{n'n''}$ | | | $|I_{n'n''}|^2$ | | |
		a	b	c	a	b	c	a	b	c
0	0	−0.9657−4	−0.9660−4	−0.9526−4	0.4073−7	0.3260−7	0.3790−7	0.9326−8	0.9331−8	0.9074−8
1	0	0.2003−4	0.2003−4	0.2338−4	−0.1240−6	−0.1291−6	−0.1187−6	0.4013−9	0.4013−9	0.5466−9
2	0	−0.1227−4	−0.1226−4	−0.1138−4	0.2730−6	0.2639−6	0.2630−6	0.1506−9	0.1504−9	0.1296−9
3	0	0.6877−5	0.6922−5	0.6868−5	−0.4996−6	−0.5503−6	−0.4829−6	0.4755−10	0.4822−10	0.4740−10
1	1	−0.9737−4	−0.9741−4	−0.9514−4	0.3773−6	0.3709−6	0.3686−6	0.9481−8	0.9488−8	0.9052−8
2	1	0.3068−4	0.3070−4	0.3548−4	−0.8309−6	−0.8451−6	−0.8203−6	0.9417−9	0.9430−9	0.1260−8
3	1	−0.2239−4	−0.2240−4	−0.2142−4	0.1520−5	0.1528−5	0.1506−5	0.5034−9	0.5043−9	0.4611−9
2	2	−0.1012−3	−0.1012−3	−0.9736−4	0.1830−5	0.1831−5	0.1811−5	0.1024−7	0.1025−7	0.9482−8
3	2	0.4195−4	0.4201−4	0.4748−4	−0.3348−5	−0.3374−5	−0.3338−5	0.1771−8	0.1776−8	0.2265−8
3	3	−0.1080−3	−0.1081−3	−0.1028−3	0.6127−5	0.6145−5	0.6105−5	0.1171−7	0.1173−7	0.1061−7

These formulas can be used to obtain any $D(k, l)\Phi(z, z')|$ from the four first members of the family, which can be expressed as

$$D(0, 0)\Phi(z, z')| = -K_0 , \qquad (73)$$

$$D(0, 1)\Phi(z, z')| = K_1/2 + \sqrt{\pi} , \qquad (74)$$

$$D(1, 0)\Phi(z, z')| = K_1/2 - \sqrt{\pi} , \qquad (75)$$

$$D(1, 1)\Phi(z, z')| = -K_2/2 + z_0 K_0 + D(0, 0)f(z, z')| , \qquad (76)$$

where K_0, K_1 and K_2 are given by

$$K_m = \int_0^{2a} du\, u^{-1/2} A(u) | . \qquad (77)$$

These integrals, which also appear in the level shift calculation, can be written in the form of infinite series of incomplete gamma functions[24]

$$K_m = \sum_{n=0}^{\infty} \gamma(3n + m + 1/2, 2az_0)/12^n n! z_0^{(3n+m+1/2)} , \qquad (78)$$

with

$$\gamma(a, x) = \int_0^x t^{a-1} \exp(-t)\, dt . \qquad (79)$$

Recurrence formulas can also be given for $D(k, l)f(z, z')|$. There are the relations

$$D(k, l)f(z, z')| = -a D(k, l-1)f(z, z')|$$

$$+ \frac{k}{4a} D(k-1, l-1)f(z, z')|$$

$$- \frac{(l-1)}{4a} D(k, l-2)f(z, z')| , \qquad (80)$$

for $l > 2$ and arbitrary k and

$$D(k, 0)f(z, z')| = -a D(k-1, 0)f(z, z')|$$

$$- \frac{(k-1)}{4a} D(k-2, 0)f(z, z')| , \qquad (81)$$

for $k > 2$. Finally

$$D(0, 0)f(z, z')| = (2a)^{-1/2} \exp\left(\frac{2a^3}{3} - 2az_0\right) . \qquad (82)$$

We have already made comparisons[5] between coupled channel and analytical results for the following parameters:

$$\mu = 7.5 \text{ aston} , \quad F = 140\,000 \text{ cm}^{-1}/\text{Å} ,$$

$$\hbar\omega = 2000 \text{ cm}^{-1} , \quad R_T(\overline{E}) = 0.062 \text{ Å} .$$

Table I is a collection of some results obtained for the same μ and ω, but F is now 60 000 cm⁻¹/Å and $R_T(\overline{E})$ is 0.066 Å. The value taken for $\hbar\omega$ is rather high and in any case much higher than the vibrational quantum of halogen molecules (Br_2, I_2, etc.), which is around 300 cm⁻¹. This choice was made because we have observed that a lower value of $\hbar\omega$ leads to an amplitude which appears as the product of a very large number by a small number, the latter coming from the near compensation of the contributions from the Airy functions on one end and from $\Phi(z, z')$ on the other. In an attempt to study I_2 with this analytical formula, we estimated that the Airy functions have to be known with more than 16 digits in order to obtain a 3 or 4 figures accuracy for $I_{n'n''}(\overline{E})$. The table presents separately the real part and the imaginary part of $I_{n'n''}(\overline{E})$ written as

$$I_{n'n''}(\overline{E}) = \Delta_{n'n''}(\overline{E}) + i\Gamma_{n'n''}(\overline{E}) . \qquad (83)$$

All amplitudes for $0 \leq n'$, $n'' \leq 3$ have been estimated. Numbers in columns (a) are from the analytical formula, in columns (b) from coupled channel equations, and in columns (c) from a semiclassical expression, the form of which will be briefly described below. The table gives also $|I_{n'n''}(\overline{E})|^2$. The potentials in the artificial channels are here taken identical to that of the excited molecule. In order for the channel functions to admit asymptotical solutions, the potentials of channels a, 2 and b are changed into constant potentials at some distance outside the interaction region. Comparison of squared moduli in columns (a) and (b) shows that the coupled channel numbers differ from the analytical results generally only by a few units in the fourth place. Thus a 3-figure accuracy is achieved with the coupled equations. A 3-figure accuracy is also obtained for the real parts of $I_{n'n''}(\overline{E})$, but the imaginary parts appear not to be reproduced with comparable accuracy. However, it must be noted that the real and imaginary parts differ in this example by 2 or 3 orders of magnitudes, so that the absolute error is about the same for the two components of the scattering amplitude. Consequently the error on the imaginary part has only a very small effect on the squared modulus.

Columns (c) of this table give the semiclassical results obtained from some formulas that we have recently proposed.[27] Although only the case of a rotationless molecule with constant electronic transition moments was discussed, it is easy to extend the scheme so as to

include centrifugal energies and varying transition moments. If the eth term of $\overline{\alpha}_{n'J',n''J''}^{\zeta\zeta}(\overline{E})$ is decomposed into its real and imaginary parts, these are given by

$$\Delta_{n'J',n''J''}^{e\zeta\zeta}(\overline{E}) = -2\pi\epsilon_{n'}\epsilon_{n''}(\overline{\omega}_{n'J'}\overline{\omega}_{n''J''})^{1/2}D_\zeta^e(R_c')D_\zeta^e(R_c'')C(\overline{E})\,|\zeta'(\overline{E})|^{1/4}\,\mathrm{Bi}(-\zeta'(\overline{E}))\,|\zeta''(\overline{E})|^{1/4}\,\mathrm{Ai}(-\zeta''(\overline{E})) \,, \quad (84)$$

$$\Gamma_{n'J',n''J''}^{e\zeta\zeta}(\overline{E}) = -2\pi\tilde{\epsilon}_{n'}\tilde{\epsilon}_{n''}(\overline{\omega}_{n'J'}\overline{\omega}_{n''J''})^{1/2}D_\zeta^e(R_c')D_\zeta^e(R_c'')C(\overline{E})\,|\zeta'(\overline{E})|^{1/4}\,\mathrm{Ai}(-\zeta'(\overline{E}))\,|\zeta''(\overline{E})|^{1/4}\,\mathrm{Ai}(-\zeta''(\overline{E})) \,. \quad (85)$$

$C(\overline{E})$ is a notation for

$$C(\overline{E}) = \{|v_R'|\,|\Delta F_R'|\,|v_R''|\,|\Delta F_R''|\}^{-1/2} \,. \quad (86)$$

In these relations quantities such as $\overline{\omega}_{n'J'}$, $|v_R'|$ and $|\Delta F_R'|$ represent a local energy spacing, a velocity, and a difference in slopes of the potentials at the pseudo-crossing point R_c.[28] This pseudocrossing point is nothing but the radiative crossing discussed in Sec. III. A symbol such as $\zeta'(\overline{E})$ represents one or the other of the two quantities

$$\zeta'^+(\overline{E}) = \pm\frac{3}{2}\left(\int_{R_T(\overline{E})}^{R_c'}|k_1|\,dR + \int_{R_c'}^{b_2'}|k_2|\,dR\right)^{2/3} \,, \quad (87)$$

or

$$\zeta'^-(\overline{E}) = \pm\frac{3}{2}\left(\int_{R_c'}^{R_T(\overline{E})}|k_1|\,dR + \int_{a_2'}^{R_a'}|k_2|\,dR\right)^{2/3} \,. \quad (88)$$

$R_T(\overline{E})$ is as defined in the analytical model, and a_2' and b_2' are the turning points of state n'. k_1 and k_2 are the wave numbers for the excited state and ground state potentials, respectively. The former form for $\zeta'(\overline{E})$ corresponds to retaining only the right turning point of the bound state function $|n'J'\rangle$, the latter to retaining only the left turning point. The $\pm$ signs correspond to bound state energies being either above or below the pseudo-crossing point energy. Finally, $\epsilon_{n'}$, $\epsilon_{n''}$, $\tilde{\epsilon}_{n'}$ and $\tilde{\epsilon}_{n''}$ in Eqs. (84) and (85) are to be taken as 1 except when $\zeta'(\overline{E})$ or $\zeta''(\overline{E})$ are calculated from Eq. (88), in which case $\epsilon_{n'} = (-1)^{n'+1}$, $\epsilon_{n''} = (-1)^{n''}$, $\tilde{\epsilon}_{n'} = (-1)^{n'}$, and $\tilde{\epsilon}_{n''} = (-1)^{n''}$. In order to incorporate into this semiclassical procedure the effect of varying the electronic transition moment, one must put as a factor its values at the pseudocrossing points. This arises in the same way as the electronic coupling calculated at the pseudo-crossing point in the level shift expression.[28]

The semiclassical results shown in Table I are seen to represent an approximation to the exact results. The differences amount in most cases only to a few percent of the scattering cross section. Such differences might be of importance in state-to-state experiments. However, such experiments do not appear to be feasible at the moment and the usual resonance Raman spectra are the superposition of such a large number of state-to-state lines that differences such as those displayed in columns (a) and (c) of Table I are unlikely to show up. This point is taken up again in the next paper, where many more comparisons of this kind are performed, in particular at the level of complete Raman profiles. Such comparisons are of great interest since the semiclassical expressions are very simple to manipulate.

VI. SOME NUMERICAL ASPECTS OF THE COUPLED CHANNEL METHOD

We would like to describe now briefly some of the numerical problems the coupled channel method is in-

volving in order to lead to results of sufficient accuracy. We consider only the asymmetrical coupling scheme, which requires less work and is as accurate as the symmetrical coupling scheme. The formula for the scattering amplitude is, from Eqs. (21), (45), and (54),

$$\mathfrak{R}_{n'J',n''J''}^e(\overline{E}) = \frac{i}{2\pi}\,e^{-i[\eta_a(\overline{E})+\eta_b(\overline{E})]}$$

$$\times S_{ba}(\overline{E})\frac{(\overline{E}-E_{n'J'}-\hbar\omega_0')(\overline{E}-E_{n''J''}-\hbar\omega_0'')}{\langle b\overline{E}|V|n'J'\rangle\langle n''J''|V|a\overline{E}\rangle} \,. \quad (89)$$

In addition to $S_{ba}(\overline{E})$, which is furnished directly by the solution of the multichannel problem, three types of quantities are needed: (a) the phases $\eta_a(\overline{E})$ and $\eta_b(\overline{E})$ in the distorted waves, which are of importance only if the phase of the scattering amplitude is needed; (b) the energy differences $(\overline{E} - E_{n'J'} - \hbar\omega_0')$ and $(\overline{E} - E_{n''J''} - \hbar\omega_0'')$. Energy $\overline{E}$ has to be closed to both $E_{n'J'} + \hbar\omega_0'$ and $E_{n''J''} + \hbar\omega_0''$ in order for the bound states to act truly as doorway states. Thus these differences must be accurately known; (c) the couplings $\langle b\overline{E}|V|n'J'\rangle$ and $\langle n''J''|V|a\overline{E}\rangle$, which for given quantum numbers have to be calculated only once, since changing the photon frequency amounts only to displacing the excited state potential. The scattering energy $\overline{E}$ can stay fixed. Independent checks can be made for all these quantities except $S_{ba}(\overline{E})$. We consider that when the conditions for integration of the coupled equations which are to be solved to obtain these auxiliary quantities are such as to provide them with a certain accuracy, a similar accuracy can be expected for $S_{ba}(\overline{E})$ under the same propagation conditions.

(a) Phases of the distorted waves

Accuracy on the phases of the distorted waves was checked by employing for the artificial potentials piecewise linear potentials which start with a slope $-F$ and become constant at some distance R_L outside the regions where the channel functions are expected to overlap. The asymptotic phase of such a potential is easily obtained from the known solutions for such a potential (Airy or sine function). This phase is given by the formula

$$\eta(\overline{E}) = \tan^{-1}[-F^{-1/3}\overline{E}^{1/2}\,\mathrm{Ai}(-\xi)/\mathrm{Ai}^{(1)}(-\xi)] - \overline{E}^{1/2}R_L \,, \quad (90)$$

where

$$\xi = F^{1/2}(R_L - R_T(\overline{E})) \,. \quad (91)$$

Table II gives an example of a study of this phase. The values labeled as η_n are obtained from a one channel calculation with various values of propagation points per wave length. This shows that a 3-figure accuracy is achieved with 24 points per wavelength, while up to 5-figure accuracy can be obtained with 50 points. However, this amounts to a large increase in computing time. Most of our calculations have been performed with 24 points. It may be noted in passing that solving

the five coupled equations to get the S matrix amounts for a rather heavy molecule like Br_2 to about half a minute of computing time on an IBM 370/168. For lighter molecules the time can be considerably reduced.

(b), (c) Energy denominators of the S matrix and couplings

An asymmetrical coupling matrix results in real poles in the S matrix, as shown by Eq. (54). The derivation of the scattering amplitude requires these denominators to be predetermined. This could be done in principle in an iterative way by first of all finding the poles, since when $\bar{E}$ approaches $E_{n'J'} + \hbar\omega_0'$ or $E_{n''J''} + \hbar\omega_0''$ (two quantities which are in principle equal but which may not be quite so from a numerical point of view), the transition probability P_{ba} should increase without limit (asymmetrical couplings producing a nonunitary S matrix, transition probabilities may assume any value). Instead of searching for the poles of the S matrix of the 5-channel problem, we analyzed some simpler 3-channel situations. When a bound state of energy E_n is placed in the position of doorway state between two continua $|1E\rangle$ and $|3E\rangle$, the transition probability $P_{31}(\bar{E})$ is given by the expression

$$P_{31}(\bar{E}) = \frac{4\Gamma_3\Gamma_1}{(\bar{E} - E_n)^2} \cdot \tag{92}$$

In Eq. (92), Γ_1 and Γ_3 are the widths the discrete level would acquire if coupled only to $|1E\rangle$ or $|3E\rangle$. Calculations with two values of $\bar{E}$ leads to the determination of both E_n and $\Gamma_3\Gamma_1$. Additional calculations leads to self-consistency checks. The examples discussed now concern the $n = 0$ or 1 levels of ground state Br_2 placed between (a) two Morse representations[27] of the $^3\Pi$ excited state; (b) a linear potential and a Morse representation of the $^3\Pi$ state; (c) two linear potentials. The channels are arranged in such a way that the real pole of Eq. (92) should always be 161.233225 cm^{-1} (zero-point level of ground state Br_2). Table III gives the poles obtained from Eq. (92), as well as the product $\Gamma_3\Gamma_1$ in each case. These products can be confronted with the values obtained from an iterative program described elsewhere[29] which determines the width and shift of molecular resonances. It is this program which is used in the determination of the couplings such as $\langle 5\bar{E}|V|n'J'\rangle$ or $\langle n''J''|V|1\bar{E}\rangle$. Thus these calculations inform us also on the reliability of coupling calculations. The table shows that errors in the location of the poles are at most $\sim 2.10^{-4}$ cm^{-1}. We may estimate now the error which is made for a given scattering energy on a cross section if instead of using the numerical pole we take it from some analytical formula. Taking for instance $\bar{E} = 161.2$ cm^{-1} gives $\bar{E} - E_n = 0.001104$ cm^{-1} if E_n is calcu-

TABLE II. Comparison of numerical and analytical estimates of a phase (in radians) of a distorted wave. n is the number of propagation points per wavelength.

n	24	30	40	50
η_n	1.980398	1.981765	1.982424	1.982600
Analytical result	$\eta = 1.982764$			

TABLE III. Poles (in cm^{-1}) of the S matrix in a 3-channel calculation with a doorway state. The analytical (exact) result is 161.233225 cm^{-1}. (i) Determination of $\Gamma_1\Gamma_3$ (in cm^{-2}) from Eq. (92). (ii) Determination of $\Gamma_1\Gamma_3$ from separate two channel calculations with determination of the widths of the resonances.

M: Morse	L: Linear	$\Gamma_3\Gamma_1$ (i)	$\Gamma_3\Gamma_1$ (ii)
	$M-M-M$		
$n=0$	161.233201	0.179544 − 2	0.179558 − 2
$n=1$	161.233013	0.169722 − 1	1.169666 − 1
	$L-M-M$		
$n=0$	161.233204	0.223257 − 1	0.223239 − 1
$n=1$	161.233040	0.587105 − 2	0.587026 − 2
	$L-M-L$		
$n=0$	161.233204	0.324685 − 2	0.324661 − 2
$n=1$	161.233040	0.194667 − 1	0.194602 − 1

lated analytically, but $\bar{E} - \bar{E}_n = 0.001090$ for the worst result of Table III ($\bar{E}_n = 161.233013$ cm^{-1}). Changing $\bar{E}_n$ into E_n affects the probabilities in such a way that

$$\frac{P_{31}}{\bar{P}_{31}} = \frac{(\bar{E} - \bar{E}_n)^2}{(\bar{E} - E_n)^2} = 0.987 \; . \tag{93}$$

Thus, a 1% error results in using the theoretical value for the pole instead of its practical value. A comparable error is to be expected on resonance Raman scattering cross sections which depend on the pole positions in a similar way.

The conclusion is that the energy denominators which are found in the elements of the S matrix can be estimated without looking first for the poles if a 3-figure accuracy only is required. It would be possible to increase the accuracy in the calculation of scattering amplitudes, but there does not seem to be any need at the moment for envisaging such more accurate (and more time consuming) determinations.

VII. CONCLUSION

Evidence has been presented that appropriate coupled channel equations can provide continuum resonance Raman scattering amplitudes with an accuracy which certainly exceed the present needs. This method, as well as the semiclassical procedure described in Sec. IV, are both used in a study of the $\Delta n = 1$ profiles of Br_2 given in the next paper.

APPENDIX: MATRIX ELEMENTS OF THE GREEN OPERATOR

The total Hamiltonian H is partitioned into H_0 defining basis functions and V responsible for inelastic scattering. In our coupling scheme the only nonvanishing elements of V are between adjacent continua (either in a symmetrical or asymmetrical way). The potentials of the various channels, the strength of the interchannel couplings, and the collision energy have been chosen in such a way that we may consider that the bound states

$|\sigma\rangle$ belonging to channel 2 ,

$|\rho\rangle$ belonging to channel 4

and the continua make up a complete basis. Let us introduce the three projection operators

$$\mathbf{P}_1 = |\rho\rangle\langle\rho| \; ; \quad \mathbf{P}_2 = |\sigma\rangle\langle\sigma| \; ; \quad \mathbf{Q} = 1 - (\mathbf{P}_1 + \mathbf{P}_2) \; . \quad (A1)$$

Starting from the definition of the Green function

$$(z - \mathbf{H})\mathbf{G}(z) = (z - \mathbf{H})(\mathbf{P}_1 + \mathbf{P}_2 + \mathbf{Q})\mathbf{G}(z) = 1 \qquad (A2)$$

with $z = \overline{E} + i\epsilon$, multiplying from the right by $\mathbf{P}_2$ and from the left successively by $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{Q}$ produce the set of equations

$$\mathbf{P}_1(z - \mathbf{P}_1\mathbf{H}_0\mathbf{P}_1)\mathbf{P}_1\mathbf{G}\mathbf{P}_2 - \mathbf{P}_1\mathbf{V}\mathbf{Q}\mathbf{G}\mathbf{P}_2 = 0 \; , \qquad (A3)$$

$$\mathbf{P}_2(z - \mathbf{P}_2\mathbf{H}_0\mathbf{P}_2)\mathbf{P}_2\mathbf{G}\mathbf{P}_2 - \mathbf{P}_2\mathbf{V}\mathbf{Q}\mathbf{G}\mathbf{P}_2 = \mathbf{P}_2 \; , \qquad (A4)$$

$$\mathbf{Q}(z - \mathbf{Q}\mathbf{H}_0\mathbf{Q})\mathbf{Q}\mathbf{G}\mathbf{P}_2 - \mathbf{Q}\mathbf{V}\mathbf{P}_1\mathbf{G}\mathbf{P}_2 - \mathbf{Q}\mathbf{V}\mathbf{P}_2\mathbf{G}\mathbf{P}_2 = 0 \; . \qquad (A5)$$

In this derivation use is made of the relations

$$\mathbf{P}_1\mathbf{H}\mathbf{P}_1 = \mathbf{P}_1\mathbf{H}_0\mathbf{P}_1 \; ; \quad \mathbf{P}_2\mathbf{H}\mathbf{P}_2 = \mathbf{P}_2\mathbf{H}_0\mathbf{P}_2 \; ,$$

$$\mathbf{P}_1\mathbf{H}\mathbf{P}_2 = 0 \; ; \quad \mathbf{Q}\mathbf{H}\mathbf{Q} = \mathbf{Q}\mathbf{H}_0\mathbf{Q} \; , \qquad (A6)$$

which result from the particular form of $\mathbf{V}$. The calculation of $\mathbf{P}_1\mathbf{G}\mathbf{P}_2$ requires elimination of $\mathbf{P}_2\mathbf{G}\mathbf{P}_2$ and $\mathbf{Q}\mathbf{G}\mathbf{P}_2$ between Eqs. (A3), (A4), and (A5). This elimination leads to

$$\mathbf{P}_2\{(z - \mathbf{P}_2\mathbf{H}_0\mathbf{P}_2 - \mathbf{P}_2\mathfrak{R}\mathbf{P}_2)$$
$$\times \mathbf{P}_2\mathfrak{R}^{-1}\mathbf{P}_1(z - \mathbf{P}_1\mathbf{H}_0\mathbf{P}_1 - \mathbf{P}_1\mathfrak{R}\mathbf{P}_1) - \mathbf{P}_2\mathfrak{R}\mathbf{P}_1\}\mathbf{P}_1\mathbf{G}\mathbf{P}_2 = \mathbf{P}_2 \; , \qquad (A7)$$

with a level-shift operator defined here as

$$\mathfrak{R} = \mathbf{V}\mathbf{Q}(z - \mathbf{Q}\mathbf{H}_0\mathbf{Q})^{-1}\mathbf{Q}\mathbf{V} \; . \qquad (A8)$$

Finally, Formula (A7) leads to

$$\langle\rho|\mathbf{G}|\sigma\rangle = \langle\rho|\mathbf{P}_1\mathbf{G}\mathbf{P}_2|\sigma\rangle$$

$$= \frac{\mathfrak{R}_{\rho\sigma}}{[z - E_{n'J'} - \hbar\omega'_0 - \mathfrak{R}_{\rho\rho}][z - E_{n''J''} - \hbar\omega''_0 - \mathfrak{R}_{\sigma\sigma}] - \mathfrak{R}_{\rho\sigma}\mathfrak{R}_{\sigma\rho}} \; . \qquad (A9)$$

Three cases can be studied:

(i) Symmetrical coupling matrix

All matrix elements of $\mathfrak{R}$ in Eq. (A9) are nonvanishing. Equation (A9) is identical to Eq. (23) if ρ is identified with $3gn'J'M'\Omega'$ and σ with $1gn''J''M''\Omega''$ and to Eq. (46) if ρ is $n'J'$ and σ is $n''J''$.

(ii) Asymmetrical coupling matrix

The diagonal elements of $\mathfrak{R}$ are zero, as well as $\mathfrak{R}_{\sigma\rho}$. Equation (A9) reduces to Eq. (54) if ρ is $n'J'$ and σ is $n''J''$. We note also that

$$\mathbf{Q}\mathbf{T}\mathbf{Q} = \mathbf{Q}\mathbf{V}\mathbf{Q} + \mathbf{Q}\mathbf{V}\mathbf{P}\mathbf{G}\mathbf{P}\mathbf{V}\mathbf{Q} = 0 \quad \text{with } \mathbf{P} = \mathbf{P}_1 + \mathbf{P}_2 \qquad (A10)$$

since

$$\mathbf{Q}\mathbf{V}\mathbf{Q} = 0 \; , \quad \mathbf{P}\mathbf{V}\mathbf{Q} \neq 0 \quad \text{but } \mathbf{Q}\mathbf{V}\mathbf{P} = 0 \; . \qquad (A11)$$

Therefore $S_{aa}(\overline{E})$, which is given by

$$S_{aa}(\overline{E}) = e^{i\eta_a(\overline{E})}[1 - 2i\pi\, T^D_{aa}(\overline{E})]\,e^{i\eta_a(\overline{E})} \; , \qquad (A12)$$

reduces to

$$S_{aa}(\overline{E}) = e^{2i\eta_a(\overline{E})} \; . \qquad (A13)$$

For the same reasons,

$$S_{33}(\overline{E}) = e^{2i\eta_3(\overline{E})} \; ; \quad S_{bb}(\overline{E}) = e^{2i\eta_b(\overline{E})} \; . \qquad (A14)$$

(iii) Asymmetrical cyclic coupling matrix

Only the off-diagonal elements of $\mathfrak{R}$ are nonzero. Equation (A9) reduces to Eq. (56) if ρ is $n'J'$ and σ is $n''J''$.

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