

## Semiclassical theory of vibrational Raman intensities

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(Received 8 June 1973; revised manuscript received 24 June 1974)

A semiclassical theory of the vibrational Raman effect based on the idea of different time scales for the electronic and nuclear motions is given. The proposed model gives a physical insight into the polarizability theory intuited by Placzek, the role of the electronic polarizability being that of the perturbation which induces first-order transition of the nuclei between vibrational levels. Extension of the semiclassical theory to the resonance Raman effect is made for the case where the intermediate states are, or may be represented by, a vibrational continuum. The specific case of the parallel components of the  $0 \rightarrow 1$  and  $0 \rightarrow 2$  Raman transitions in  $H_2^+$  is considered.

## I. INTRODUCTION

Despite a number of recent theoretical studies, the Raman effect<sup>1</sup> still often suffers from rather complex discussions in which the actual physical process undergone by the molecule remains to some extent, obscured. We present here a consideration of the Raman effect<sup>2,3</sup> based on the use of different time scales for the electronic and nuclear motions, and implemented with the semiclassical theory of radiation. The model provides an insight into the nature of the Raman process and for the nonresonance case gives a physical justification of the polarizability theory of Placzek.<sup>4</sup> The quantitative accuracy of the polarizability theory will be shown, both formally and by example to be reasonably good, in some cases, even at resonance. The present discussion builds on a previous study<sup>5</sup> which considered the validity of the polarizability theory from a mathematical point of view, and specifically dealt with the static limit,  $\omega_0 \rightarrow 0$ . Those ideas are readily extended here to the frequency-dependent case including the resonance Raman effect.

The role in the Raman process played by the electric polarizability tensor  $\tilde{\alpha}_{cl}$ , parametric in the nuclear coordinates  $Q$ , is not usually fully developed. For example, the standard textbook discussions are given not in terms of  $\tilde{\alpha}_{cl}$ , but rather its derivatives ("derived polarizabilities"), which is unenlightening from the viewpoint of the physics of the phenomenon since they are only indirectly related to the perturbing operators and are completely insufficient at electronic resonance where the selection rules break down. A somewhat different viewpoint of the Raman process can be attained by foregoing the customary Herz-

berg-Teller expansions<sup>6</sup> which lead to the Taylor series for  $\tilde{\alpha}_{cl}$ , and leaving this quantity intact. Unlike uv spectroscopy where these expansions are introduced to treat the nuclear motion as a perturbation, in the Raman effect the nuclear motion is the phenomenon itself.

The essence of the Raman effect can be seen by considering a homonuclear diatomic molecule perturbed by the classical radiation field associated with the photons (were a permanent dipole moment present, its contribution would merely be projected out in the ensuing formalism). Initially, with the field absent the nuclei move in the Born-Oppenheimer (BO) or adiabatic<sup>7</sup> potential given by the ground-state electronic eigenvalue,  $E_0(R)$ , parametric in  $R$ . In the electric field  $\vec{F}$  of the radiation the electronic eigenvalue is perturbed by the amount  $-\frac{1}{2}\vec{F} \cdot \tilde{\alpha}_{cl}(R, \omega_0) \cdot \vec{F}$ <sup>8</sup> and so the nuclei experience a perturbation equal to this value and undergo a *first-order* transition from initial vibrational state  $\chi_{oi}$  to final state  $\chi_{of}$ , both of the electronic ground state. The transition amplitude is proportional to the matrix element  $\langle \chi_{of} | \tilde{\alpha}_{cl}(R, \omega_0) | \chi_{oi} \rangle_R \equiv \tilde{\alpha}_{if}(BO, \omega_0)$  which can be shown by ready extension of the method of Ref. 5 employed for the static case to be a very good approximation to the exact transition amplitude, denoted  $\tilde{\alpha}_{if}(\omega_0)$ .<sup>9</sup> What we are saying is that in the spirit of the BO approximation the slowly moving nuclei experience the radiation indirectly through the second-order optical perturbations (parametric in  $R$ ) of the electrons. Since the electrons move much more rapidly, their response to the external field is relatively rapid and they, in turn, or more precisely their shift in energy serves as the actual perturbation experienced by the nuclei. The nuclear transition, then, is essentially a first-order

process despite the fact that the radiation field interaction is second order.

The proposed model gives an explanation of the role of the electronic polarizability in the Raman effect more than does the usual classical description based on radiation from an induced oscillating dipole moment coupled to the vibrations. Here, the polarizability enters as the actual perturbation that effects a vibrational transition.

Our discussion will be developed in the following way. Section II contains the semiclassical, multi-time-scale argument which furnishes the vibronic transition amplitude as  $\bar{\alpha}_{if}(\text{BO}, \omega_0)$ . Extension of the use of  $\bar{\alpha}_{if}(\text{BO}, \omega_0)$  to the resonance Raman effect is considered in Sec. III A and is illustrated with explicit calculations on the  $\text{H}_2^+$  molecule ion in Sec. III B.

Although we will not consider the diagonal case ( $i=f$ ) for the molecular polarizability explicitly, it should be clear that the analogous quantity  $\bar{\alpha}_{ii}(\text{BO}, \omega_0) \equiv \langle \chi_{0i} | \bar{\alpha}_{ei}(R, \omega_0) | \chi_{0i} \rangle$  will furnish the cross section for Rayleigh scattering or the probability that the molecule remains in its initial vibronic state. All the results obtained for the accuracy of the Raman matrix element  $\bar{\alpha}_{if}(\text{BO}, \omega_0)$  apply to the molecular polarizability as well where the approximation is commonly termed "vibrational averaging."

## II. SEMICLASSICAL MODEL OF THE VIBRATIONAL RAMAN EFFECT

In this section we develop the theory of the Raman effect employing arguments based, for simplicity, on the case of a homonuclear diatomic molecule. From the previous discussion we begin by solving the electronic problem, holding the nuclei fixed at various values of the internuclear separation  $R$ . The incident and scattered radiation are treated semiclassically in the dipole approximation by means of two electric fields,<sup>10</sup>  $\vec{F}_0$  and  $\vec{F}_s$  with frequencies  $\omega_0$  and  $\omega_s$ , and we seek the change in electronic energy,  $\Delta E(R, t)$ , which is parametric in  $R$ . Now the electronic energy in the presence of the two fields, a "pseudoeigenvalue" since it is time dependent, can be expanded in a perturbation series in the electric field strengths  $F_0$  and  $F_s$  and the bilinear term<sup>11</sup> will turn out to contain a contribution equal to the electronic polarizability times a frequency factor  $e^{-i(\omega_0 - \omega_s)t}$ , where the frequency difference  $\omega_0 - \omega_s$  corresponds to a vibronic excitation energy  $W_{0f} - W_{0i}$  (the first and second indices of  $W$  designate, respectively, the electronic and vibrational quantum numbers).

At some later time the nuclear problem can be considered to begin, with the nuclei initially in state  $\chi_{0i}$  experiencing this harmonic perturbation

bilinear in the field strengths. A simple variation-of-constants treatment of the vibrational Schrödinger equation demonstrates that a first-order transition  $\chi_{0i} - \chi_{0f}$ , with amplitude proportional to the matrix element  $\bar{\alpha}_{if}(\text{BO}, \omega_0)$ , will ensue.

Consider, then, the electronic Hamiltonian  $\mathcal{H}_{el}$  of a homonuclear diatomic molecule (ion) in the presence of two electric fields, which may be written as

$$\mathcal{H}_{el}(\boldsymbol{r}, R, \omega_0, \omega_s, t) = H_{el}(\boldsymbol{r}, R) + H^{1,0}(\boldsymbol{r}, \omega_0, t) + H^{0,1}(\boldsymbol{r}, \omega_s, t), \quad (1)$$

where  $\boldsymbol{r}$  symbolizes the electronic coordinates  $\vec{r}_i$  measured from the center of mass of the nuclei and  $H_{el}$  is the field-free electronic Hamiltonian (including nuclear repulsion) in a molecule-fixed coordinate system. The interaction energies between the electrons and the incident and scattered radiation (the nuclei-field interaction energies being much smaller) are given by

$$H^{1,0} = -\vec{r} \cdot \vec{e}_0 F_0 (e^{i\omega_0 t} + e^{-i\omega_0 t}) \quad (2a)$$

and

$$H^{0,1} = -\vec{r} \cdot \vec{e}_s F_s (e^{i\omega_s t} + e^{-i\omega_s t}), \quad (2b)$$

respectively, where  $-\vec{r}$  symbolizes the electronic dipole operator  $-\sum_i \vec{r}_i$  in atomic units (used throughout) and  $\vec{e}_0$  and  $\vec{e}_s$  are unit vectors in the respective directions of incident and scattered polarization.

The ground-state electronic wave function  $\Psi_{el}(\boldsymbol{r}, R, \omega_0, \omega_s, t)$  is the solution to the time-dependent Schrödinger equation

$$[\mathcal{H}_{el}(\boldsymbol{r}, R, \omega_0, \omega_s, t) - i(\partial/\partial t)] \Psi_{el}(\boldsymbol{r}, R, \omega_0, \omega_s, t) = 0, \quad (3)$$

satisfying the initial conditions

$$\Psi(\boldsymbol{r}, R, \omega_0, \omega_s, t \rightarrow -\infty) = \varphi_0(\boldsymbol{r}, R) e^{-iE_0(R)t} \equiv \Psi_{el}^0(\boldsymbol{r}, R, t), \quad (4)$$

where

$$\langle \Psi_{el}^0 | \Psi_{el}^0 \rangle = 1,$$

and the unperturbed ground-state wave function and corresponding eigenvalue are obtained from

$$H_{el} \varphi_0 = E_0 \varphi_0. \quad (5)$$

It is convenient to write  $\Psi_{el}$  as<sup>12</sup>

$$\begin{aligned} \Psi_{el}(\boldsymbol{r}, R, \omega_0, \omega_s, t) = & a_0(R, \omega_0, \omega_s, t) \\ & \times \varphi(\boldsymbol{r}, R, \omega_0, \omega_s, t) e^{-iE_0(R)t}, \end{aligned} \quad (6)$$

where  $a_0 = \langle \Psi_{el}^0 | \Psi_{el} \rangle$ , a function of  $\varphi$ , takes care of

secular and normalization terms while  $\varphi$  deals with the physics of the perturbation problem. The latter is obtained by solving

$$[H_{el} + H^{1,0} + H^{0,1} - E_0 - \Delta E - i(\partial/\partial t)]\varphi = 0, \quad (7)$$

with the initial condition  $\varphi(r, R, \omega_0, \omega_s, -\infty) = \varphi_0(r, R)$ , and having for later times the intermediate normalization  $\langle \varphi_0 | \varphi \rangle = \langle \varphi_0 | \varphi_0 \rangle = 1$ . The desired time-dependent perturbation energy is obtained from the equation

$$\Delta E = \langle \varphi_0 | H^{1,0} + H^{0,1} | \varphi \rangle, \quad (8)$$

and, in particular, the desired bilinear term is found after making the expansions

$$\varphi = \varphi_0 + F_0 \varphi^{1,0} + F_s \varphi^{0,1} + F_0 F_s \varphi^{1,1} + \dots \quad (9)$$

and

$$E = E_0 + F_0 E^{1,0} + F_s E^{0,1} + F_0 F_s E^{1,1} + \dots \equiv E_0 + \Delta E, \quad (10)$$

and substituting these into Eq. (7). This yields the sequence of decoupled equations

$$[H_{el} - E_0 - i(\partial/\partial t)]\varphi^{1,0} = \vec{r} \cdot \vec{e}_0 (e^{i\omega_0 t} + e^{-i\omega_0 t}) \varphi_0, \quad (11a)$$

$$[H_{el} - E_0 - i(\partial/\partial t)]\varphi^{0,1} = \vec{r} \cdot \vec{e}_s (e^{i\omega_s t} + e^{-i\omega_s t}) \varphi_0, \quad (11b)$$

$$[H_{el} - E_0 - i(\partial/\partial t)]\varphi^{1,1} = \vec{r} \cdot \vec{e}_0 (e^{i\omega_0 t} + e^{-i\omega_0 t}) \varphi^{0,1} + \vec{r} \cdot \vec{e}_s (e^{i\omega_s t} + e^{-i\omega_s t}) \varphi^{1,0} + E^{1,1} \varphi_0, \quad (12)$$

etc. Clearly  $E^{0,1} = E^{1,0} = 0$  since the molecule possesses no permanent dipole moment.

Equations (11a), (11b), and (12) may be readily solved with the *ansatz*

$$\varphi^{1,0} = \varphi_+^{1,0} e^{i\omega_0 t} + \varphi_-^{1,0} e^{-i\omega_0 t}, \quad (13a)$$

$$\varphi^{0,1} = \varphi_+^{0,1} e^{i\omega_s t} + \varphi_-^{0,1} e^{-i\omega_s t}, \quad (13b)$$

$$\varphi^{1,1} = \varphi_{++} e^{i(\omega_0 + \omega_s)t} + \varphi_{+-} e^{i(\omega_0 - \omega_s)t} + \varphi_{-+} e^{i(\omega_s - \omega_0)t} + \varphi_{--} e^{-i(\omega_0 + \omega_s)t}, \quad (13c)$$

and

$$E^{1,1} = E_{++} e^{i(\omega_0 + \omega_s)t} + E_{+-} e^{i(\omega_0 - \omega_s)t} + E_{-+} e^{i(\omega_s - \omega_0)t} + E_{--} e^{-i(\omega_0 + \omega_s)t}. \quad (14)$$

Now of the terms on the right-hand side of Eq. (14), with  $\omega_0 > \omega_s$  the third term will give rise to (Stokes) absorption  $\chi_{0i} \rightarrow \chi_{0f}$  since  $\omega_0 - \omega_s \approx W_{0f} - W_{0i}$ , while the second term corresponds to (anti-Stokes) emission,  $\chi_{0f} \rightarrow \chi_{0i}$ . The remaining terms correspond to two photon processes and need not be considered further. Then for absorption we need only evaluate  $E_{-+}$ , which serves as the  $R$ -

dependent part of the harmonic nuclear perturbation (which we now consider to be turned on). This is accomplished by solving Eqs. (15a)–(15c),

$$[H_{el} - E_0 - \omega_0] \varphi_-^{1,0} = \vec{r} \cdot \vec{e}_0 \varphi_0, \quad (15a)$$

$$[H_{el} - E_0 + \omega_s] \varphi_+^{0,1} = \vec{r} \cdot \vec{e}_s \varphi_0, \quad (15b)$$

and

$$[H_{el} - E_0 + \omega_s - \omega_0] \varphi_{-+} = \vec{r} \cdot \vec{e}_0 \varphi_+^{0,1} + \vec{r} \cdot \vec{e}_s \varphi_-^{1,0} + E_{-+} \varphi_0, \quad (15c)$$

via expansions in the unperturbed electronic states  $\varphi_n$ . We obtain

$$\varphi_-^{1,0} = \sum_{n \neq 0} \frac{\varphi_n \langle \varphi_0 | \vec{r} \cdot \vec{e}_0 | \varphi_n \rangle}{E_n - E_0 - \omega_0}, \quad (16a)$$

$$\varphi_+^{0,1} = \sum_{n \neq 0} \frac{\varphi_n \langle \varphi_0 | \vec{r} \cdot \vec{e}_s | \varphi_n \rangle}{E_n - E_0 + \omega_s}, \quad (16b)$$

which, on substitution into (15c) yields

$$E_{-+} = - \sum_{n \neq 0} \langle \varphi_0 | \vec{r} \cdot \vec{e}_s | \varphi_n \rangle \langle \varphi_n | \vec{r} \cdot \vec{e}_0 | \varphi_0 \rangle \times [(E_n - E_0 - \omega_0)^{-1} + (E_n - E_0 + \omega_s)^{-1}]. \quad (17)$$

Aside from the over-all sign difference owing to the definition of a polarizability,  $E_{-+}(R, \omega_0, \omega_s)$  is just an element of the dynamic electronic polarizability tensor  $\vec{\alpha}_{el}(R, \omega_0, \omega_s)$ , the two frequencies arising from the two energy denominators of Eq. (17). This appears to be the appropriate form for the semiclassical theory of the Raman effect, but  $\vec{\alpha}_{el}(R, \omega_0)$  is a good approximation to it.

Having evaluated the relevant component of  $\Delta E$ , we may now insert the perturbation  $E_{-+} F_0 F_s$  into the nuclear Schrödinger equation

$$[T_R + E_0 + E_{-+} F_0 F_s e^{-i\omega t} - i(\partial/\partial t)]\chi(R, t) = 0, \quad (18)$$

which may be solved by the variation-of-constants method, writing

$$\chi(R, t) = \sum_k b_k(t) \chi_{0k}(R) e^{-iW_{0k}t}, \quad (19)$$

with initial conditions  $b_k(0) = \delta_{k0}$ . As is well known, there will be a large probability of transition if  $\omega \approx \omega_0 - \omega_s = W_{0f} - W_{0i}$ , which is the case here by construction. The expression for the transition probability,  $P_{if}$ , is, after time integration,

$$tP_{if} = |b_f(t)|^2 = 4 |\langle \chi_{0i} | E_{-+}(R, \omega_0, \omega_s) | \chi_{0f} \rangle|^2 F_0^2 F_s^2 \times \left( \frac{\sin[\frac{1}{2}(W_{0f} - W_{0i} - \omega)t]}{(W_{0f} - W_{0i} - \omega)} \right)^2. \quad (20)$$

Then from our discussion of the approximate equality of  $-E_{-+}$  and  $\vec{\alpha}_{el}(R, \omega_0)$  we have the desired result, that  $P_{if}$  is proportional to the square of  $\vec{\alpha}_{if}(R, \omega_0) = \langle \chi_{0i} | \vec{\alpha}_{el}(R, \omega_0) | \chi_{0f} \rangle$ , with  $\vec{F}_0 \cdot \vec{\alpha}_{el} \cdot \vec{F}_s$

playing the role of an effective first-order perturbation. As has been pointed out previously<sup>5,9</sup>  $\bar{\alpha}_{if}(\text{BO}, \omega_0)$  is nearly equal to  $\bar{\alpha}_{if}(\omega_0)$  since the former approximate quantity just derived here can also be obtained from the dispersion-equation expression for the exact matrix element  $\bar{\alpha}_{if}(\omega_0)$  by keeping only the leading term latter energy-denominator expansion and performing closure over intermediate vibrational states. Thus, the present time-dependent treatment has derived not only the Placzek polarizability result, but also a good approximation to the exact transition probability. In this context it is perhaps worth noting that a variation-of-constants treatment employing two perturbing fields and the exact molecular wave functions<sup>13</sup> leads to an expression for  $P_{if}$  similar to Eq. (20) where the exact molecular polarizability, dependent on  $\omega_0$  and  $\omega_s$ , replaces the matrix elements of  $\bar{\alpha}_{ei}(R, \omega_0, \omega_s)$ .

### III. RESONANCE RAMAN EFFECT

#### A. Theory

Because of the growing experimental importance of the resonance Raman effect and the simplicity of the semiclassical polarizability theory, it is of interest to see that in some instances, at least, the latter may be readily adapted to the resonance problem. When resonance irradiation takes place via a repulsive electronic state, or via a bound state above its dissociation limit (or if the intermediate contribution can be treated as if it were from a continuum)  $\alpha_{if}^{pp}(\omega_0)$  is given by (neglecting small terms from electronic states not at resonance)

$$\alpha_{if}^{pp}(\omega_0) = \int_0^\infty \alpha_{if}^{pp}(W_{nk}, \omega_0) \rho(W_{nk}) dW_{nk}, \quad (21)$$

where

$$\alpha_{if}^{pp}(W_{nk}, \omega_0) = \frac{\langle \chi_{oi} | f_n^p | \chi(W_{nk}) \rangle_R \langle \chi(W_{nk}) | f_n^p | \chi_{of} \rangle_R}{W_{nk} - W_{oi} - \omega_0}. \quad (22)$$

(Small terms with  $+\omega_0$  energy denominators are also neglected here.) The initial and final vibrational functions,  $\chi_{oi}$  and  $\chi_{of}$ , and the continuum functions  $\chi(W_{nk}, R)$  having a density  $\rho(W_{nk})$  and written simply as  $\chi(W_{nk})$  are solutions to the nuclear Schrödinger equation

$$[T_R + E_e(R) - W_{ev}] \chi_{ev} = 0 \quad \text{for all } e, v. \quad (23)$$

The transition dipole moment matrix element for the electronic ground state  $\varphi_0$  and intermediate electronic state  $\varphi_n$  is defined by

$$f_n^p(R) = \langle \varphi_0 | r_p | \varphi_n \rangle_r.$$

Now using the function<sup>14(a)</sup>

$$\zeta(x) = \lim_{\gamma_t \rightarrow 0} (x + i\gamma_t)^{-1} = P_x - i\pi\delta(x), \quad (24)$$

and identifying  $x$  with  $W_{nk} - W_{oi} - \omega_0$ , Eq. (21) can be written as<sup>14(b)</sup>

$$\alpha_{if}^{pp}(\omega_0) = P \int_0^\infty \alpha_{if}^{pp}(W_{nk}, \omega_0) \rho(W_{nk}) dW_{nk} - i\pi \langle \chi_{oi} | f_n^p | \chi(W_{nk}^*) \rangle \langle \chi(W_{nk}^*) | f_n^p | \chi_{of} \rangle \rho(W_{nk}^*), \quad (25)$$

where  $W_{nk}^* = W_{oi} + \omega_0$  corresponds to the resonance condition. Now the principal part of Eq. (25) still admits closure since the only values of  $W_{nk}$  which have been removed from the integral make no contribution as the integrand is odd-valued about  $W_{nk}^*$ . Thus, the expansion of  $[W_{nk} - W_{oi} - \omega_0]^{-1}$  about  $[E_n(R) - E_0(R) - \omega_0]^{-1}$  [Ref. 5, Eq. (14)] is at least formally valid, furnishing the leading term

$$\int_0^\infty \chi_{oi} f_n^p (E_n - E_0 - \omega_0)^{-1} f_n^p \chi_{of} dR.$$

This integrand itself also possesses a pole, namely, at that value  $R^*$  for which  $E_n(R^*) - E_0(R^*) - \omega_0 = 0$ , and in analogy we may attempt to write

$$\alpha_{if}^{pp}(\text{BO}, \omega_0) = P \int_0^\infty \chi_{oi} f_n^p (E_n - E_0 - \omega_0)^{-1} f_n^p \chi_{of} dR - i\pi \chi_{oi}(R^*) f_n^p(R^*) f_n^p(R^*) \chi_{of}(R^*). \quad (26)$$

It is of interest to ask whether the principal parts and residues of Eqs. (25) and (26) correspond. This is certainly plausible in the case of the residues since the approximation of  $\chi(W_{nk}^*)$  by a  $\delta$  function at the classical turning point  $R_c$  of  $E_n$  is usually quite adequate<sup>15</sup> and  $R_c \approx R^*$  [the  $\delta$ -function normalization takes care of the density of states in Eq. (25)]. That the principal parts of  $\bar{\alpha}_{if}(\omega_0)$  and  $\bar{\alpha}_{if}(\text{BO}, \omega_0)$  are also approximately equal in at least one system is illustrated in Sec. III B.

#### B. An example: Resonance Raman effect in $\text{H}_2^+$

The parallel component of the  $\text{H}_2^+$  Raman matrix element,  $\alpha_{of}^{\parallel} \equiv \alpha_{of}^{xx}$ , for transition between the vibrational ground state (0) and final vibrational state ( $f$ ), both of the electronic ground state ( $1s\sigma_g$ ), provides a convenient test of the previous arguments for the resonance Raman effect. In this case the intermediate electronic state  $\varphi_n = 2p\sigma_u$  provides the contribution to Eq. (25) (it is essentially the sole contributor even in the static limit) and its electronic energy is the repulsive potential for the intermediate continuum functions  $\chi(W_{nk})$ .

In order to evaluate Eqs. (25) and (26) for the

exact and polarizability theoretic values of the Raman matrix element for various  $\omega_0$ ; it was necessary to obtain accurate values of  $E_0(R)$ ,  $E_n(R)$  (here,  $n=1$ ),  $f_1^e(R)$  and to obtain the bound and continuum vibrational states,  $\chi_{0a}$  ( $a=0, 1, 2$ ) and  $\chi(W_{1k})$ , with respective energies  $W_{0a}$  and  $W_{nk}$ . These quantities are illustrated in Fig. 1.

The electronic energies were obtained by fitting<sup>16</sup> the  $E_0$  values of Wind<sup>17</sup> and the  $E_1$  values of Peek.<sup>18</sup> The transition dipole matrix elements  $f_n^e(R)$  were computed by fitting the linear-combination-of-atomic-orbitals (LCAO) values obtained previously<sup>5</sup> with three significant-figure agreement with the results of Bates.<sup>19</sup> Bound and continuum vibrational wave functions and energies were obtained by solving the equation

$$\left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + E_e(R)\right) \chi_{ev} = W_{ev} \chi_{ev},$$

for  $e=0, v=0, 1, 2$  and  $e=1, v=k$  using the Numerov-Cooley procedure.<sup>20</sup> For convenience the  $\chi(W_{1k})$  were normalized in a box of length  $R=50 a_0$  corresponding to the energy interval ca. 0.003 a.u. Technically speaking, the  $\chi$  are discrete ( $\chi_{1k}$  in previous notation). However, it was verified that the  $\chi$  tended to  $\sin(kR + \delta)/k$  for large  $R$ .

To economize on computer time, not all of the set of  $\chi$  was generated—only about 40% in the Franck-Condon region, and  $300\chi_{1k}$  in all. Instead, a density of states  $\rho(w_{1k})$  was obtained by counting the nodes of each  $\chi_{1k}$  and assigning  $\rho(W_{1k})=1$  if the state  $\chi_{1,k+1}$  was present,  $\rho(W_{1k})=2$  if  $\chi_{1,k+1}$  was absent but  $\chi_{1,k+2}$  was present, etc. The adequacy

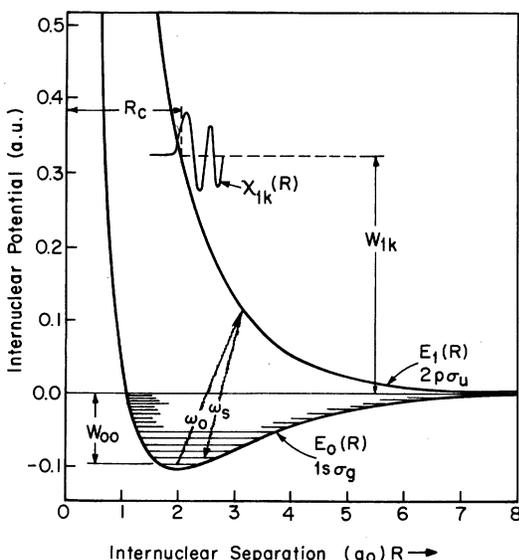


FIG. 1.  $1s\sigma_g(E_0)$  and  $2p\sigma_u(E_1)$  potential curves of  $H_2^+$  plotted as a function of internuclear separation. Quantities appearing in Eqs. (25) and (26) are depicted.

of this procedure was then tested by numerous sum rules, e.g.,

$$\langle \chi_{00} | (f_1^e)^2 | \chi_{00} \rangle_R = \int dW_{1k} \rho(W_{1k}) \langle \chi_{00} | f_1^e | \chi(W_{1k}) \rangle_R \times \langle \chi(W_{1k}) | f_1^e | \chi_{00} \rangle_R, \quad (27)$$

which would be satisfied exactly for a complete set of intermediate states. Evaluation of the two sides of Eq. (27) by numerical integration using Simpson's rule gave agreement to four decimal places.

Table I contains the principal parts of  $\alpha_{0f}^{ee}(\omega_0)$  and  $\alpha_{0f}^{ee}(\text{BO}, \omega_0)$  for the  $f=1$  and  $f=2$  cases at eight resonance frequencies, evaluated from Eqs. (25) and (26). Included in the table are the corresponding values of  $R^*$  and it can be seen that all the important regions of  $R$  space are represented. The values of  $\alpha_{01}^{ee}$  and  $\alpha_{02}^{ee}$  are seen to be extremely rapidly varying functions of  $\omega_0$ , particularly for resonance in the vicinity of the  $E_0$  minimum where there is even a change in sign. Nonetheless,  $\alpha_{0f}^{ee}(\text{BO}, \omega_0)$  is reasonably close to  $\alpha_{0f}^{ee}(\omega_0)$  in almost every instance.<sup>21</sup> Notice also that for the static limit ( $\omega_0=0$  or  $R^*=\infty$ )  $\alpha_{01}^{ee} \gg \alpha_{02}^{ee}$  confirming the selection rules, but that this is not true for the resonance case. In fact, in a number of instances the 0-3, 0-4, etc., transitions will have similarly large amplitudes for certain  $\omega_0$  values.

The residues which correspond to these principal parts are very small and it will be sufficient to give a few values. The sum-over-states and BO residues corresponding to  $R^*=2.0 a_0$  are  $-5.3 \times 10^{-3}$  and  $-6.6 \times 10^{-3} a_0^3$ , respectively for  $\alpha_{01}^{ee}(\omega_0)$  while for  $\alpha_{02}^{ee}(\omega_0)$  they are  $-8.1 \times 10^{-3}$  and  $-7.0 \times 10^{-3}$ . These were the largest residues found, as they drop off rapidly with increasing distance from  $R^*=2.0$  a.u.

The results of this section then imply that the polarizability theory has application to the resonance Raman effect as well as the nonresonance case.

TABLE I. Principal parts of  $\alpha_{01}^{ee}(\omega_0)$  and  $\alpha_{02}^{ee}(\omega_0)$  given by the sum-over-states<sup>a</sup> and semiclassical<sup>b</sup> expressions for several values of the resonance frequency  $\omega_0$ .

$\omega_0$ (a.u.)	$R^*(a_0)^c$	$\alpha_{01}^{ee}(\omega_0)$	$\alpha_{01}^{ee}(\text{BO}, \omega_0)$	$\alpha_{02}^{ee}(\omega_0)$	$\alpha_{02}^{ee}(\text{BO}, \omega_0)$
0	$\infty$	1.993	1.997	0.158	0.160
0.021	6.0	2.00	2.01	0.159	0.165
0.101	4.0	2.30	2.35	0.270	0.307
0.145	3.5	2.76	2.88	0.485	0.610
0.208	3.0	4.60	5.00	1.93	2.02
0.305	2.5	5.30	5.27	-9.34	-9.49
0.431	2.0	-13.7	-12.7	9.69	10.2
0.621	1.5	1.90	1.25	-1.09	-2.34
0.887	1.0	0.183	0.177	-0.078	-0.072

<sup>a</sup> Equation 25.

<sup>b</sup> Equation 26.

<sup>c</sup> Value of  $R$  at which  $E_1(R) - E_0(R) = \omega_0$ . See also Ref. 21.

## IV. CONCLUSIONS

The present discussion of the vibrational Raman effect has furnished a physical model giving a somewhat new quantum-mechanical role to the electronic polarizability in the phenomenon. The notion of events on two different time scales has been invoked, this being in accord with the general discussion of time-independent phenomena given by the Born-Oppenheimer approximation and the Hellmann-Feynman theorem, with the electrons said to be moving far more rapidly than the nuclei and contributing in an averaged manner to the potential and forces, respectively, experienced by the nuclei.

The semiclassical result has also been shown

to have application to the resonance case when the intermediate states are, or can be represented by, a molecular vibronic continuum. The detailed conditions for the success of the semiclassical theory to hold at resonance are to some extent still open, particularly where resonance occurs through discrete intermediate states. There, it appears that the damping constant, which for the continuum case may be neglected, need be included.

## ACKNOWLEDGMENTS

The authors wish to acknowledge support from the Alfred P. Sloan Foundation and the National Science Foundation (Grant No. GP 29554).

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‡Taken in part from the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn for the degree Doctor of Philosophy (chemical physics).

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<sup>8</sup>Actually, the semiclassical perturbation theory of Sec. II requires two slightly different fields,  $\vec{F}_0$  and  $\vec{F}_s$ , whose beats perturb the nuclei. The term  $\vec{F}_0 \cdot \vec{\alpha}_{el} \cdot \vec{F}_s$  therefore oscillates about a time-averaged  $\vec{F}_{av} \cdot \vec{\alpha}_{el} \cdot \vec{F}_{av}$ ; however, the oscillations are of crucial importance.

<sup>9</sup>The static case,  $\omega_0 = 0$ , is very similar to the situation far from resonance. As resonance via bound intermediate vibronic states is approached the polarizability approximation becomes increasingly poor as was shown in the case of  $H_2$  by A. L. Ford and J. C. Browne, *Phys. Rev.* **7**, 418 (1973) and also A. L. Ford, Ph.D. thesis (University of Texas, 1972) (unpublished). (This work also contains a numerical example of the accuracy of

the polarizability result in the static case for  $H_2$ , which parallels the numerical results of Ref. 5 for  $H_2^+$ ). The situation near resonance when intermediate continuum states are involved exclusively has not been studied and may be amenable to the polarizability approximation as is the Raman effect at resonance described in Sec. III.

<sup>10</sup>By invoking two fields we do not mean to imply a stimulated Raman effect, but rather, as with a quantized radiation treatment wish to enable various time orderings of absorption and emission, recognizing the deficiencies of semiclassical theory for spontaneous emission.

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<sup>21</sup>The somewhat larger error for  $\omega_0 = 0.621$  appears to be due to the use of  $R^* = 1.5a_0$  rather than the appropriate value,  $1.51a_0$ . This demonstrates the care which must be taken in extracting the principal parts of Eqs. (25) and (26) from the nearly cancelling large positive and negative contributions on either side of the pole.