some power is lost by doubling the frequency to the green, the stimulated Raman effect can often be obtained by the green pulses. The combination of frequency broadening and dispersion becomes more favorable for the green pulse train.[21]

Experiments, both with the Nd^{3+}-glass laser and a ruby laser, are now in progress. More detailed information could be obtained with the use of a second cell as a picosecond pulse amplifier. The influence of a variable delay time between the laser and Stokes pulse and the influence of phase distortion caused by dispersion could then be made more quantitative.

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Selection Rules and the Protonic Spectrum of Molecules*

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Recently, we have reported variational solutions to Schrödinger's equation for CH_4, NH_3, H_2O, and HF, using a Hamiltonian which included the kinetic-energy operators of the protons. The results of these calculations implied the existence of protonic spectra similar to the electronic spectra. We show here that the selection rules which apply to electrons also apply to the protons. Furthermore, we find a two-particle-transition operator which allows an electron and a proton or two protons to be simultaneously excited with intensities proportional to the square of km_p/M, where k is the wave number of the light, m_p is the mass of the proton, and M is the total mass of the molecule. For completeness, the effects of the radiation field on the coordinates of the c.m. are given also.

I. INTRODUCTION

Recently we have reported variational solutions to Schrödinger's equation for CH_4, NH_3, H_2O, and HF using a Hamiltonian which included the kinetic energies of the protons.[1,2] The trial wave function was an expansion of the form

$$\psi = \sum_i \sum_a C_{ia} F_i G_{a'} \quad , \tag{1}$$

where for n electrons and m protons, we have

$$F=\frac{1}{\sqrt{n!}}\det|f_1(1)\cdots f_n(n)| \qquad (2)$$

and
$$G=\frac{1}{\sqrt{m!}}\det|g_1(1)\cdots g_m(m)| \ . \qquad (3)$$

The f's represent one-electron functions and the g's represent one-proton functions. The energy spectrum which we got for the protons was similar to the usual electronic spectrum. Hence, we would expect that there should exist electric dipole, electric quadrupole, magnetic dipole, and higher-order transitions involving only protons in the same way as they exist for electrons. It is the purpose of this paper to show that these transitions are allowed for the protons and that their intensities are comparable to those found for electrons.

II. SELECTION RULES

The Hamiltonian for a molecule in a classical radiation field is

$$H=\sum_j\left[\frac{1}{2m_j}\left(\frac{\hbar}{i}\vec{\nabla}_j-\frac{q_j}{c}\vec{A}_j\right)^2+q_j\phi_j\right]+V ,$$

where q_j is the charge of the jth particle, $\vec{A}_j$ and ϕ_j are the vector and scalar potentials, and V is the potential representing the interaction among the particles in the molecule. In the Coulomb gauge $\vec{\nabla}\cdot\vec{A}=0$, and the Hamiltonian becomes

$$H=\sum_j\left(\frac{-\hbar^2}{2m_j}\nabla_j^2+\frac{iq_j\hbar}{m_jc}(\vec{A}_j\cdot\vec{\nabla}_j)+\frac{q_j^2A_j^2}{2m_j}+q_j\phi_j\right)+V .$$

The scalar potential may be omitted because the radiation field can be described by the vector potential. The square of the vector potential may be neglected because it is small when compared with $\vec{A}_j\cdot\nabla_j$ for the radiation fields which we will consider. Therefore, the Hamiltonian which we will use is

$$H=H_0+H' ,$$

where
$$H_0=\sum_j\left[\frac{-\hbar^2}{2m_j}\nabla_j^2\right]+V ,$$

and
$$H'=\sum_j\frac{iq_j\hbar}{m_jc}\vec{A}_j\cdot\vec{\nabla}_j .$$

We will solve Schrödinger's equation using $H_0^{\prime}$ only to get the unperturbed solutions by transforming H_0 to c.m. coordinates defined by the relations

$$\vec{R}=\frac{m_a\vec{r}_a+\sum_j\vec{r}_j}{m_a+\sum_jm_j},\qquad \vec{R}_j=\vec{r}_j-\vec{r}_a ,\qquad j\neq a ,$$

where the r's represent position vectors in the laboratory coordinate system. Particle a (usually the most massive) has been selected as the origin of the relative coordinate system. The transformed H_0 is

$$H_0=-\frac{\hbar^2}{2M}\nabla_R^2-\sum_j\left(\frac{\hbar^2}{2\mu_j}\nabla_j^2\right)-\frac{\hbar^2}{m_a}\left(\sum_j\sum_{k>j}\vec{\nabla}_k\cdot\vec{\nabla}_j\right)+V ,$$

where now the sums over j or k exclude $j=a$ or $k=a$, $M=m_a+\sum_jm_j$, and $\mu_j=m_jm_a/(m_j+m_a)$. The set of unperturbed eigenfunctions will be represented by

$$\Psi_n=\Phi(\vec{R})\psi_n(\vec{R}_1,\ldots,\vec{R}_t) \ . \qquad (4)$$

A perturbation calculation leads to the following integral:

$$H'_{nm}=\int\Psi_n^*\sum_j\left(\frac{iq_j\hbar}{m_j}\vec{A}_j\cdot\vec{\nabla}_j\right)\Psi_m dV \ . \qquad (5)$$

In what follows, we will assume that the size of the molecule is much smaller than the wavelength of the radiation. We will consider a plane wave traveling in the x direction with $\vec{A}$ in the z direction. Thus,

$$A_z=\frac{1}{c}\left(A_0e^{i(kx-\nu t)}+A_0^*e^{-i(kx-\nu t)}\right),$$

where k is the wave number. With this A_z, Eq. (5) becomes

$$H'_{nm}=\frac{1}{c}\int\Psi_n^*\sum_r\left(\frac{i\hbar q_r}{m_r}[A_0e^{i(kx_r-\nu t)}+A_0^*e^{-i(kx_r-\nu t)}]\frac{\partial}{\partial z_r}\right)\Psi_m dV \ .$$

This integral can be rewritten

$$H'_{nm}=\frac{1}{c}\left(e^{-i\nu t}A_0\alpha'_{nm}+e^{i\nu t}A_0^*\alpha'^*_{nm}\right),$$

where
$$\alpha'_{nm}=\int\Psi_n^*\left(\sum_r\frac{i\hbar q_r}{m_r}e^{ikx_r}\frac{\partial}{\partial z_r}\right)\Psi_m dV \ .$$

Since our wave function is in c.m. coordinates, we need to transform the operator in α'_{nm} to the same coordinates. We will make use of the following relations:

$$\vec{r}_j=\left(1-\frac{m_j}{M}\right)\vec{R}_j+\vec{R}-\sum_{k\neq j}\frac{m_k}{M}\vec{R}_k,$$

and
$$\vec{r}_a=\vec{R}-\sum_j\frac{m_j}{M}\vec{R}_j \ .$$

With these relations, we find that

$$\frac{q_r}{m_r}e^{ikx_r}\frac{\partial}{\partial z_r}=\exp\left\{ik\left[\left(1-\frac{m_r}{M}\right)X_r+X-\sum_{s\neq r}\frac{m_s}{M}X_s\right]\right\}\times\left(\frac{q_r}{m_r}\frac{\partial}{\partial Z_r}+\frac{q_r}{M}\frac{\partial}{\partial Z}\right),$$

and

$$\frac{q_a}{m_a}e^{ikx_a}\frac{\partial}{\partial z_a}=\exp\left\{ik\left[X-\sum_r\frac{m_r}{M}X_r\right]\right\}$$

$$\times\left[\frac{q_a}{M}\frac{\partial}{\partial Z}-\sum\nolimits_r\frac{q_a}{m_a}\frac{\partial}{\partial Z_r}\right].$$

Therefore, α'_{nm} becomes

$$\alpha'_{nm}=\sum\nolimits_r\int\Psi_n^*\exp\left[ik\left(X-\sum_{s\neq r}\frac{m_s}{M}X_s\right)\right]$$

$$\times i\hbar\left[\left(\frac{q_r}{m_r}\exp\left[ik\left(1-m_r/M\right)X_r\right]\right.\right.$$

$$\left.-\frac{q_a}{m_a}\exp\left[-ik(m_r/M)X_r\right]\right)\frac{\partial}{\partial Z_r}$$

$$+\{\exp[ik(1-m_r/M)X_r]-\exp[-ik(m_r/M)X_r]\}$$

$$\left.\times\frac{q_r}{M}\frac{\partial}{\partial Z}\right]\Psi_m d\vec{R}\,d\vec{R}_1\ldots d\vec{R}_t\,, \tag{6}$$

where we have made use of the relation $q_a=-\sum_r q_r$. Since $kX_r\ll 1$ and $m_r/M<1$, we can use the following approximations for the exponentials:

$$\exp[ik(1-m_r/M)X_r]\approx 1+ik(1-m_r/M)X_r\,, \tag{7}$$

$$\exp[ik(m_r/M)X_r]\approx 1-ik(m_r/M)X_r\,, \tag{8}$$

$$\exp[-ik\sum\nolimits_s(m_s/M)X_s]\approx 1-ik\sum\nolimits_s(m_s/M)X_s\,. \tag{9}$$

Note that m_r/M will be essentially zero for electrons, but for the protons its value will not be negligible in general. If we take the first term of each of the power series and use Eq. (4), we get

$$\alpha'_{nm}\approx\int\Phi^*(\vec{R})e^{ikX}\Phi(\vec{R})\,d\vec{R}$$

$$\times\sum\nolimits_r\int\psi_n^*\left[i\hbar\left(\frac{q_r}{m_r}-\frac{q_a}{m_a}\right)\frac{\partial}{\partial Z_r}\right]\psi_m d\vec{R}_1\cdots d\vec{R}_t\,.$$

The integral over the coordinates of the c. m. is the same for all transitions, so we may as well define α_{nm} to be α'_{nm} divided by that integral. Then

$$\alpha_{nm}=-i\nu_{nm}\sum\nolimits_r\int\psi_n^*\left[\left(\frac{q_r}{m_r}-\frac{q_a}{m_a}\right)\mu_r Z_r\right]\psi_m d\vec{R}_1\cdots d\vec{R}_t\,,$$

where $h\nu_{nm}=E_n-E_m$ and $\mu_r=m_r m_a/(m_a+m_r)$. When we add and subtract q_r/m_a to the expression in parenthesis, we get

$$\alpha_{nm}=-i\nu_{nm}\int\psi_n^*\left[\sum\nolimits_r\left(1-\frac{\mu_r}{m_a}-\frac{q_a\mu_r}{q_r m_a}\right)q_r Z_r\right]$$

$$\times\psi_m d\vec{R}_1\cdots d\vec{R}_t\,. \tag{10}$$

For electrons $\mu_r/m_a\approx 0$, so, the operator reduces to the usual $\sum_r q_r Z_r$; however, for protons, the same ratio is not negligible. For example, in ammonia $m_a\approx 25\,000$ and $\mu_r\approx 1700$, so $\mu_r/m_a\approx 0.07$ and $q_a\mu_r/q_r m_a\approx 0.49$. Therefore, the factor in the parentheses is about 0.4. However, the average value of Z_r for the protons is about 2.0 bohr which when multiplied by 0.4 gives 0.8. The value of this product is close to the average value of Z_r for the electrons, which is about 0.5. It appears that the intensities which are proportional to the square of α_{nm} will be roughly the same for both types of transitions.

When the product $\psi_n^*\psi_m$ is even, the integral involving the Z_r (or any odd operator) will vanish. When this happens, we can consider the second terms in the expansions (7) and (8) and the first term of expansion (9) to get

$$\alpha_{nm}=-\int\psi_n^*\left[k\hbar\sum\nolimits_r\left(\frac{q_r}{m_r}-\frac{q_r}{M}+\frac{q_a m_r}{m_a M}\right)X_r\frac{\partial}{\partial Z_r}\right]$$

$$\times\psi_m d\vec{R}_1\cdots d\vec{R}_t\,. \tag{11}$$

The term involving $\partial/\partial Z$ in Eq. (6) vanishes because the integral $\int\psi_n X_r\psi_m d\vec{R}_1\cdots d\vec{R}_s$ vanishes, since we said that $\psi_n^*\psi_m$ is even. We can neglect all the terms in the square brackets except for q_r/m_r for electrons. Since the charge of most nuclei is about one-half their atomic number, $q_a/m_a\approx\frac{1}{2}m_p$, where m_p is the mass of the proton. Therefore, for protons we find that the last two terms are approximately equal to $-\frac{1}{2}M$. In the molecules that we considered $M\approx 15\,m_p$; therefore, for protons the term in square brackets is approximately $(1.0-0.3)/m_p=0.97/m_p$. We see that for protons the effect of the additional terms is small, but not negligible. Note that for any molecule where $q_r=q_a$ and $m_r=m_a$, the term in square brackets reduces to q_r/m_r. The integral given by Eq. (11) will give the quadrupole moment operator and the magnetic dipole operator in the usual way. That is,

$$\alpha_{nm}=-i\nu_{nm}k\int\psi_n^*(\sum\nolimits_r\mu_r K_r X_r Z_r)\,\psi_m d\vec{R}_1\cdots d\vec{R}_t$$

for electric quadrupole radiation, and

$$\alpha_{nm}=-\nu_{nm}k\int\psi_n^*(\sum\nolimits_r K_r L_{yr})\,\psi_m d\vec{R}_1\cdots d\vec{R}_t$$

for magnetic dipole radiation, where K_r is the factor in parenthesis in Eq. (11) and L_y is the angular momentum operator.

We will now consider the second term of expansion (9) using the first terms of expansions (7) and (8). The integral is

$$\alpha_{nm}=\int\psi_n^*\left[\sum_r\left(-ik\sum_{s\neq r}\frac{m_s}{M}X_s\right)\right.$$

$$\left.\times i\hbar\left(\frac{q_r}{m_r}-\frac{q_a}{m_a}\right)\frac{\partial}{\partial Z_r}\right]\psi_m d\vec{R}_1\cdots d\vec{R}_t\,.$$

We can safely neglect all the terms in the sum over s where s refers to an electron. Therefore, from now on the sum over s is restricted to protons only, and

$$\alpha_{nm}=-i\nu_{nm}k\left(\frac{m_p}{M}\right)$$

$$\times \int \psi_n^* \Big(\textstyle\sum_r \sum_{s \neq r} Q_r Z_r X_s \Big) \psi_m \, d\vec{\mathrm{R}}_1 \cdots d\vec{\mathrm{R}}_t \,, \tag{12}$$

where $$Q_r = q_r \;\; 1 - \frac{\mu_r}{m_a} - \frac{q_a \mu_r}{q_r m_a} \quad . \tag{13}$$

We have said that $m_p/M \approx 0.07$. Therefore, the intensities of these transitions are roughly $\frac{1}{200}$ as intense as the electric-quadrupole or magnetic-dipole transitions. The $Z_r X_s$ operator is a two-particle operator which involves two protons or a proton and an electron.

We will now substitute for ψ_n and ψ_m functions of the form defined by Eq. (1) into Eq. (10). Let

$$D_z = D_{zp} + D_{ze}, \text{ where } D_{zp} = \textstyle\sum_A Q_A Z_A$$

and $D_{ze} = \sum_I Q_I Z_I$,

and where Q_A and Q_I are defined by Eq. (13) and Z_A and Z_I are the Z coordinates of the Ath proton and the Ith electron in the c. m. system. We want to find the allowed transitions for electric dipole radiation between ψ and ψ', where

$$\psi = \textstyle\sum_i \sum_a C_{ia} F_i G_a \text{ and } \psi' = \sum_i \sum_a C'_{ia} F_i G_a \,.$$

Therefore, we need to know the conditions under which

$$P_z = \int \Psi D \, \Psi' d\, V \neq 0,$$

$$= \textstyle\sum_i \sum_a \sum_j \sum_b C^*_{ia} \, C'_{jb} \int F^*_i G^*_a D_z F_j G_b dV,$$

$$= \textstyle\sum_i \sum_a \sum_j \sum_b C^*_{ia} C'_{jb} \big(\int F^*_i D_{ze} F_j dV_e$$

$$\times \int G^*_a G_b dV_p + \int F^*_i F_j dV_e \int G^*_a D_{zp} G_b dV_p \big) \,,$$

but F_i is orthogonal to F_j and G_a is orthogonal to G_b; therefore,

$$P_z = \textstyle\sum_i \sum_j \sum_a C^*_{ia} C'_{ja} \int F^*_i D_{ze} F_j dV_e$$

$$+ \textstyle\sum_a \sum_b \sum_i C^*_{ia} C'_{ib} \int G^*_a D_{zp} G_b dV_p \,.$$

Since D_{ze} and D_{zp} are odd operators, $F^*_i F_j$ and $G^*_a G_b$ must also be odd if the integrals are not to vanish. This requirement gives the usual selection rules for dipole moment transitions. Note that we can have transitions which involve only electrons, only protons, or both protons and electrons. A similar development can be made for the electric quadrupole moment and the magnetic dipole moment simply by substituting the corresponding operators. Equation (12), however, leads to a different result as we shall now show. Let

$$\textstyle\sum_r \sum_{s \neq r} Q_r Z_r X_s = \sum_I \sum_A Q_I Z_I X_A + \sum_A \sum_{B \neq A} Q_A Z_A X_B \,,$$

where I refers to the electrons and A and B refer to protons. The integral in equation (12) becomes

$$\textstyle\sum_i \sum_a \sum_j \sum_b C^*_{ia} C'_{ib} \int F^*_i G^*_a \big(\sum_I \sum_A Q_I Z_I X_A \big) F_j G_b dV_e dV_p + \sum_a \sum_b \sum_i C^*_{ia} C'_{ib} \int G^*_a \big(\sum_A \sum_{B \neq A} Q_A Z_A X_B \big) G_b dV_p \,.$$

The first integral in expression (14) becomes

$$\big(\textstyle\sum_I Q_I \int F^*_i Z_I F_j dV_e \big) \big(\sum_A \int G^*_a X_A G_a dV_p \big).$$

Each of these integrals are nonvanishing only when the selection rules for electric dipole radiation are satisfied by at least one electron and at least one proton. Their polarizations are in different directions. The same result is obtained for the second integral in expression (14), but in this case two protons simultaneously are excited subject to the selection rules of electric dipole transitions.

We can make some general remarks on the dependence of

$$Q_r = q_r \left(1 - \frac{\mu_r}{m_a} - \frac{q_a \mu_r}{q_r m_a} \right), \quad \text{and} \quad K_r = \frac{q_r}{m_r} - \frac{q_r}{M} + \frac{q_a m_r}{m_a M}$$

on m_a and M, which apply to protons.; if $m_a = m_r$ and $q_a = q_r$; $Q_r = 0$ and $K_r = q_r/m_r$. As m_a increases, Q_r tends to q_r; and K_r tends to q_r/m_r. If M increases while m_a remains the same, Q_r remains the same and K_r becomes again q_r/m_r.

The intensities of the transitions allowed by the two particle operator in Eq. (12) decrease as M increases. For example, these transitions in NH_3 would be 300 times more intense than they would be for UH_3.

So far we have avoided looking at the effects of the radiation field on the coordinates of the c. m. We will now do so. Let $\Phi_{\vec{K}}(\vec{R}) = \exp(i \vec{K} \cdot \vec{R})$. The effect of an operator on Φ is $A \Phi_{\vec{K}} = \phi_{\vec{K}}$,

where $\phi_{\vec{K}} = \int a_{\vec{K}\vec{K}'} \Phi_{\vec{K}'} d\vec{K}'$;

then $$\int \Phi^*_{\vec{K}''} A \, \Phi_{\vec{K}} dV = \int \Phi^*_{\vec{K}''} \int a_{\vec{K}\vec{K}'} \Phi_{\vec{K}'} d\vec{K}' dV$$

$$= \int a_{\vec{K}\vec{K}'} \int \Phi_{\vec{K}''} \Phi_{\vec{K}'} dV d\vec{K}'$$

$$= \int a_{\vec{K}\vec{K}'} \delta(\vec{K}' - \vec{K}'') d\vec{K} = a_{\vec{K}\vec{K}''} .$$

The two operators which involve the coordinates of the center of mass are e^{ikX} and $(\hbar/iM) \, e^{ikX} \partial/\partial Z$. For the first of these operators we have

$$a_{\vec{K}\vec{K}'}=\int_{-\infty}^{\infty} e^{i(K_X+k-K_X')X}\,dX\,\delta(K_Y-K_Y')\,\delta(K_Z-K_Z')$$

$$=\delta(K_X+k-K_X')\,\delta(K_Y-K_Y')\,\delta(K_Z-K_Z')$$

$$\approx\delta(\vec{K}-\vec{K}')\ ,$$

since k is much smaller than K_X. This result merely states there will be essentially no change in the momentum of the center of mass, and whatever change there is will be in the X component of the momentum. The second operator gives

$$a_{\vec{K}\vec{K}'}=\frac{\hbar}{iM}\int_{-\infty}^{\infty} e^{-iK_Z'Z}\,\frac{\partial}{\partial Z}\,e^{iK_ZZ}\,dZ\,\delta(K_X+k-K_X')\,\delta(K_Y-K$$

$$=(\hbar K_Z/M)\,\delta(K_Z-K_Z')\,\delta(K_X+k-K_X')\,\delta(K_Y-K_Y')$$

$$\approx v_Z\,\delta(\vec{K}-\vec{K}')$$

since $\hbar K_Z$ is the momentum in the Z direction.

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Resonant Scattering of Radiation from Collision-Damped Two-Level Systems

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The power spectrum of the radiation emitted by a driven collision-damped two-level system is evaluated. The driving field, which is treated classically, is assumed to oscillate harmonically near the atomic resonance frequency, and its intensity is allowed to assume arbitrary values. The collisions are assumed to be strong, i.e., to instantaneously thermalize the state of the atom. The limiting forms of the power spectrum of the radiated field are discussed for the cases of low and high excitation of the atomic system.

I. INTRODUCTION

The effect of collisions on the response of a collection of atoms to a monochromatic incident electromagnetic field has been extensively studied, in both classical and quantum-mechanical contexts.[1-8] For the most part, previous analyses have been devoted to the evaluation of quantities which depend only upon the mean values of atomic operators, such as the electromagnetic susceptibilities or the absorption line-shape function, i.e., the rate of attenuation of the incident field as a function of its frequency. It has been found, in particular, that the widths[9] of the peaks (centered at the atomic resonance frequencies) in the line-shape function are proportional to the collision rate for relatively weak incident fields, but that they are proportional to the intensity of the incident field when it is great enough to lead to an appreciable degree of saturation.

In the present paper our interest lies in describing the spectral properties of the field radiated by the driven atoms, and hence in evaluating the correlation function which represents the product of atomic dipole moments at two different times. We assume that the incident field oscillates at a fixed frequency ω which lies near an atomic resonance frequency ω_0, and allow the field intensity to be arbitrarily great. Our analysis is carried out within the context of a simple model consisting of a single two-level atom driven by a classical electric field and subject to strong random collisions which abruptly thermalize its state. We assume that the collision rate κ is much greater than all other relaxation rates, in particular, that it is much greater than the radiative decay rate, the effect of which has been analyzed in a previous paper.[10]

The results we find for the case of collisional relaxation differ markedly in the limit of weak driving fields from those for the case of radiative relaxation. A principal difference is that in the collisional case the radiated field contains, in addition to a coherent monochromatic spectral component oscillating at the driving frequency ω, incoherent components oscillating within an in-