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Time-resolved luminescence from coherently excited molecules as a probe of molecular wave-packet dynamics

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We calculate the time-dependent spectrum of spontaneously emitted light from a coherently excited diatomic molecule. We show that this spectrum provides a tool for direct observation of the atomic vibrations in the excited electronic state of the molecule, and that the finite time and frequency resolution inherent in any experiment does not destroy all information about the time-dependent shape of the molecular wave packet.

I. INTRODUCTION

Recent progress in subpicosecond laser spectroscopy has allowed studies of several ultrafast atomic and molecular processes and is pursued actively in many laboratories. Many examples of measurements in the time domain can be given that were possible only in the frequency domain until recently.[1-7] The time-resolved measurements often provide new insight into physical and chemical processes,[8,9] even if they cannot improve the accuracy of the determination of atomic constants.

Application of ultrashort pulses to the excitation of quantum systems allows the generation of wave packets, i.e., coherent superpositions of eigenstates. The wave packets are well localized in space, and their time evolution is a quantum counterpart of the classical evolution of the system. In the present paper we discuss the wave packets formed by a superposition of several vibrational states in molecules. Previous works have shown experimentally that it is possible to create such wave packets using femtosecond-duration laser pulses and to detect them by probing the time-dependent absorption[2,3] or Stokes shift of a second probe pulse,[4] or by monitoring the total[1] or the frequency-resolved[9] fluorescence from a transition state during photodissociation. Such effects can also occur in the solid state. For example, Jansky, Meceski, and Vinogradov[10] have predicted that coherent phonon excitation in crystals will lead to a time-dependent hot-luminescence spectrum. In this paper we will deal solely with the observation of the spontaneous emission of light from a coherently excited diatomic molecule, addressing the questions of how one defines an experimental time-dependent spectrum, and to what extent the measurement reflects the shape of the molecular nuclear wave packet.

In order to visualize how atomic oscillations can manifest themselves in spontaneously emitted light, let us perform a simplified analysis of the process. The potential curves of an exemplary diatomic molecule (here Na_2) for the ground and excited state are shown in Fig. 1(a). The exciting pulse of very short duration creates a coherent superposition of vibrational eigenstates in the excited electronic state. The wave packet formed in such a way will begin to oscillate between the classical turning points of the potential, imitating the motion of a classical particle. Such a wave packet is a source of spontaneously emitted light. In fact, at any moment of time the molecule can emit a photon. Depending on the instantaneous

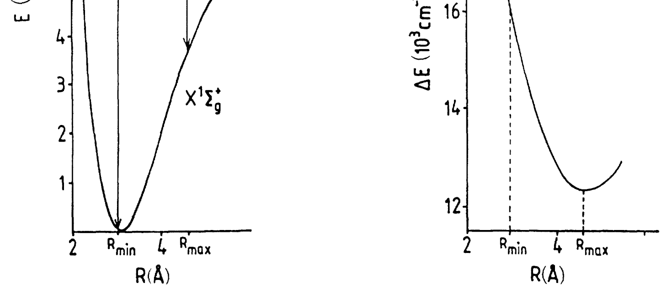

FIG. 1. (a) Potential-energy curves for the Na_2 molecule in the ground and excited states, as a function of the internuclear separation. (b) Difference of the ground- and excited-state potentials.

position of the atoms relative to each other, the frequency of the emitted photons will change in time according to the Franck-Condon principle [see Fig. 1(a)]. Therefore, by measuring the spectral decomposition of radiation at each moment of time, one can follow the oscillations of the atoms.

This idea is attractive; but first, we will have to define what we mean by the spectrum of light emitted at a given time. In the standard formulation of a spectral decomposition, there is no place for time dependence. This point will be discussed in detail in Sec. II. In Sec. III we will discuss the process of coherent excitation and subsequent spontaneous emission of radiation from a diatomic molecule. Section IV contains results of the numerical calculations for a specific example of the Na_2 molecule.

II. TIME-DEPENDENT SPECTRUM

It is well known that the Weiner-Khintchine definition of the power spectrum of a random process holds only for stationary processes. Therefore, the concept of a time-dependent spectrum must be more clearly defined. From the physical point of view, the *energy* spectrum for a finite time duration can be measured, and a time-dependent spectrum with some physical meaning may be defined on this basis. The pioneering paper of Eberly and Wodkiewicz[11] introduced a definition of the time-dependent spectrum which is both mathematically rigorous and follows from a possible physical measurement. Moreover, this paper stressed the necessity of linking the notion of the time-dependent spectrum to the specific physical experiment. Our definition of the time-dependent spectrum, although somewhat different from the one given in Ref. 11, originates from similar physical considerations.

Consider an electric-field pulse $E(t)$, whose time-dependent spectrum we wish to determine. The first step toward defining this quantity will be to define the time duration for which the radiation is detected. The pulse will go through a device, the time gate, which will leave the field unchanged for times around some time T (the moment that the time gate is opened). Before $T-1/2\Gamma$, as well as after $T+1/2\Gamma$ (where Γ is a parameter of the gate), the time gate is closed, i.e., the electric field is not transmitted. This means that the electric field, after passing through the time gate, is given by

$$E_B(t)=E(t)B(t,T) , \tag{1}$$

where $B(t,T)$ is a function describing the gate. Several models of the function $B(t,T)$ are possible; for instance,

$$B(t,T)=\exp\{-[(t-T)\Gamma]^2\} . \tag{2}$$

In most of this paper, however, we will use a different choice:

$$B(t,T)=\exp(-|t-T|\Gamma) , \tag{3}$$

for which the calculations turn out to be simpler.

The next step is to introduce a frequency filter that represents the action of a spectrometer. This filter does exactly the same to the electric field in the frequency domain as the time gate does in the time domain. In other words, the field $E(\omega)$, after passing through a frequency filter, becomes

$$E_F(\omega)=E(\omega)H(\omega,\omega_F) . \tag{4}$$

The function $H(\omega,\omega_F)$ transmits frequencies close to the central frequency of the pulse ω_F with resolution γ. A possible choice of function H, used also in Ref. 11, is

$$H(\omega,\omega_F)=\gamma^2[\gamma^2+(\omega-\omega_F)^2]^{-1} . \tag{5}$$

The formula for the electric field, after going through the frequency filter, can be written in the time domain as

$$E_F(t)=\int_{-\infty}^{t} dt' H(t-t',\omega_F)E(t'), \tag{6}$$

where

$$H(t,\omega_F)=\frac{1}{2\pi}\int d\omega \exp(-i\omega t)H(\omega,\omega_F) . \tag{7}$$

Combining the time gate and the frequency filter, we find that after passing through the time gate B, and subsequently by the frequency filter H, the electric field $E(t)$ becomes

$$E_{FB}(t)=\int_{-\infty}^{t} dt' H(t-t',\omega_F)B(t',T)E(t') . \tag{8}$$

Finally, we introduce our definition of the time-dependent spectrum of the field $E(t)$. By definition, the energy spectrum of the field $E(t)$ measured at the time T and at the frequency ω_F is the total energy transmitted through the time gate and the frequency filter:

$$S(T,\omega_F)=\int_{-\infty}^{\infty} dt|E_{FB}(t)|^2 . \tag{9}$$

As seen from this definition, the spectrum $S(T,\omega_F)$ depends not only on the time T and the frequency ω_F, but on the widths of the two filters as well.

This is the main result of this section. The time-dependent spectrum $S(T,\omega_F)$, as introduced here, is based on the analysis of a possible experiment. Different experiments may measure different time-dependent spectra. Our definition differs, for example, from the Eberly-Wodkiewicz time-dependent spectrum. However, our choice is the one that is most commonly used in subpicosecond measurements.

III. TIME-DEPENDENT SPECTRUM OF LIGHT EMITTED BY A DIATOMIC MOLECULE

A. Coherent excitation of the molecule

Consider a diatomic molecule in its ground electronic state and in its lowest vibrational state when irradiated by a short laser pulse. The light pulse will lead to the coherent excitation of several vibrational levels in the upper electronic state. After the excitation, the wave function may be found by solving the Schrödinger equation. This is most conveniently written for the probability amplitudes c_α and c_n for finding the molecule in the appropriate state:

$$i\frac{d}{dt}c_n=E_nc_n+\sum_{n,\alpha}E(t)d_{n\alpha}c_\alpha\ ,$$
$$i\frac{d}{dt}c_\alpha=E_\alpha c_\alpha+\sum_{n,\alpha}E(t)d_{\alpha n}c_n\ . \tag{10}$$

Here $E(t)$ denotes the electric-field envelope of the exciting pulse. The vibrational levels in the ground state are labeled by n ($n=1,2,\ldots$) and in the excited state by α ($\alpha=1,2,\ldots$), where $E_{n,\alpha}$ are the eigenenergies and $d_{n\alpha}$ are the dipole matrix elements between the vibrational levels of the ground and excited electronic states. The molecule is assumed to be a homonuclear one; thus $d_{nn}=0=d_{\alpha\alpha}$.

Equations (10) can be easily solved for a given shape of the exciting pulse with the help of perturbation theory. We will discuss the case of a Gaussian pulse. Thus the electric field is

$$E(t)=E_0\exp(-i\omega_Lt-t^2/\tau^2)+\text{c.c.} \tag{11}$$

The parameter τ determines the pulse duration. For such a pulse shape, we find that, for times $t\gg\tau$, the amplitudes c_α are

$$c_\alpha(t)=-i(\pi\tau^2)^{1/2}E_0d_{\alpha0}\times\exp[-iE_\alpha t-(E_\alpha-E_0-\omega_L)^2\tau^2/4]\ . \tag{12}$$

Here, E_α and E_0 denote the energies of the vibrational level α in the excited electronic state and the ground vibrational level in the ground electronic state. These amplitudes, at the time just after the pump pulse has passed, will be the starting point for our analysis of the emitted radiation. The relevant amplitudes will be denoted as $c_\alpha(0)$, and the wave function will be taken as

$$\psi(0)=\sum_\alpha\psi_\alpha c_\alpha\ . \tag{13}$$

Subsequent time evolution of the amplitudes takes a simple form:

$$c_\alpha(t)=\exp(-iE_\alpha t)c_\alpha(0)\ . \tag{14}$$

This formula does not include radiative damping. Since we will be interested in evolution during times that are short compared with collisional as well as radiative damping, there is no need to discuss it further.

B. Spontaneous emission of light from a coherently excited molecule

The molecule excited to the state $\psi(0)$ is a source of radiation at later times. The radiation originates from the transitions to the ground electronic state. Since several vibronic states are involved in the upper state, as well as lower states, the steady-state spectrum consists of many sharp lines.

The time-dependent spectrum, as defined in Sec. II, can be easily calculated. The source of the field is provided by (virtual) dipole transitions to the ground electronic state. The electric-field operator $E(t)$ in the far field is proportional to the transition dipole moment operator $d(t)$. Thus the measured time-dependent spectrum is given by

$$S(T,\omega_F)=\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\int_{-\infty}^{t}dt''H^*(t-t',\omega_F)\times B(T,t')H(t-t'',\omega_F)\times B(T,t'')\langle d(t')d(t'')\rangle\ . \tag{15}$$

The quantum expectation value, denoted by $\langle\ \rangle$, is to be taken over the initial state $\psi(0)$. The two-time dipole-dipole correlation function in the above formula can be written as

$$\langle d(t)d(t')\rangle=\sum_{\alpha,\beta,n}c_\alpha^*(0)c_\beta(0)d_{n\alpha}d_{\beta n}\exp[-i(E_\alpha-E_n)t]\times\exp[-i(E_n-E_\beta)t']\ . \tag{16}$$

With the choice of the time gate function $B(t,T)=\exp(-|t-T|\Gamma)$, and the frequency filter function $H(\omega,\omega_F)=\gamma^2[\gamma^2+(\omega-\omega_F)^2]^{-1}$, we can perform all the time integrals exactly. The result is

$$\begin{aligned}S(t,\omega_F)={}&\sum_{n,\alpha,\beta}c_\alpha^*c_\beta d_{\alpha n}d_{n\beta}\exp[-i(E_\alpha-E_\beta)T]\\&\times\left[\frac{1}{2\Gamma-i(E_\alpha-E_\beta)}\frac{1}{\gamma+\Gamma+i(E_n+\omega_0-E_\alpha)}\frac{1}{\gamma+\Gamma-i(E_n+\omega_0-E_\beta)}\right.\\&+\frac{1}{2\Gamma+i(E_\alpha-E_\beta)}\frac{1}{\gamma-\Gamma+i(E_n+\omega_0-E_\alpha)}\frac{1}{\gamma-\Gamma-i(E_n+\omega_0-E_\beta)}\\&+\frac{-2\Gamma}{[\gamma-i(E_n+\omega_0-E_\beta)]^2-\Gamma^2}\frac{1}{\gamma-\Gamma+i(E_n+\omega_0-E_\alpha)}\frac{1}{\gamma+\Gamma+i(E_n+\omega_0-E_\alpha)}\\&+\frac{-2\Gamma}{[\gamma+i(E_n+\omega_0-E_\alpha]^2-\Gamma^2}\frac{1}{\gamma-\Gamma-i(E_n+\omega_0-E_\beta)}\frac{1}{\gamma+\Gamma-i(E_n+\omega_0-E_\beta)}\\&\left.+\frac{1}{2\gamma}\frac{4\Gamma^2}{[\gamma+i(E_n+\omega_0-E_\alpha)]^2-\Gamma^2}\frac{1}{[\gamma-i(E_n+\omega_0-E_\beta)]^2}\right]\ .\end{aligned} \tag{17}$$

This is the final expression for the time-dependent spectrum of spontaneously emitted light from a coherently excited molecule. We will apply and discuss it in more detail in Sec. IV, when we consider a specific example.

IV. DISCUSSION AND EXPERIMENTAL CONSIDERATIONS

We supplement the general calculation given above by calculations for a specific molecule that is Na_2. Consider a sodium molecule prepared in the lowest vibrational level of the ground electronic state (e.g., by supersonic expansion). The molecules are excited by a Fourier-limited Gaussian pulse of 50 fs duration (spectral width of about 600 cm^{-1}) and central wavelength $\lambda = 630$ nm. The pulse is split into a pump pulse and a suitably delayed auxiliary pulse. The pump pulse excites the molecule from the $v'' = 0$ vibrational level in the ground $X\,^1\Sigma_g^+$ state to a coherent superposition of several vibrational levels in the $A\,^1\Sigma_u^+$ state centered at $v' = 10$. As explained in Sec. III, such an excitation scheme leads to a wave packet $\psi(0)$ in the $A\,^1\Sigma_u^+$ state centered around the distance of the equilibrium position of the $X\,^1\Sigma_g^+$ state. This position is also the inner turning point for the subsequent oscillation of the wave packet. The resulting $A\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$ fluorescence emitted in the forward direction is analyzed by an ultrafast temporal gate. The gate is opened by the auxiliary pulse (using, for example, the up-conversion technique pioneered by Mahr and Hirsch[12]) suitably delayed by time T. The temporal width of the time gate is equal to the duration of the auxiliary pulse. The gated fluorescence is resolved spectrally by a monochromator.

We have calculated the spectrum of the gated fluorescence as a function of the time delay T using the formula (17). The vibrational wave functions necessary for the calculation of $d_{n\alpha}$ and c_α were obtained by solving the appropriate radial Schrödinger equation numerically, using the method described by Cooley.[13] The potential-energy curves for the states $X\,^1\Pi_g^+$ and $A\,^1\Sigma_u^+$ are taken from Kush and Hessel[14] and Gerber and Möller.[15] We assumed that the electronic part of the transition dipole moment does not depend substantially on the internuclear distance R, which is a reasonable approximation for the limited range of R sampled by the wave packet. Note once more that for the sake of simplicity the temporal integrals in (17) were evaluated with pulses of two-exponential form rather than with the Gaussian pulses assumed for the excitation. This introduces only a minor change in the final results.

Figure 2 displays the spectra of the gated fluorescence calculated for the gate positions $T = 0$ (300), 37, 75, 112, and 150 fs relatively to the pump pulse. These time delays correspond to 0, (t_{vib}), $t_{\text{vib}}/8$, $t_{\text{vib}}/4$, $3t_{\text{vib}}/8$, and $t_{\text{vib}}/2$, where t_{vib} denotes the period of vibrational oscillations of the A-state wave packet. According to the classical picture, at a given moment of time T, the molecule emits photons with energy equal to the difference of potential energies at the internuclear distance $R(T)$, at which the wave packet is currently positioned [Fig. 1(a)]. As the difference potential for the $A\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$ transition changes by as much as 4000 cm^{-1} in the range of R sampled by the wave packet, the fluorescence spectrum

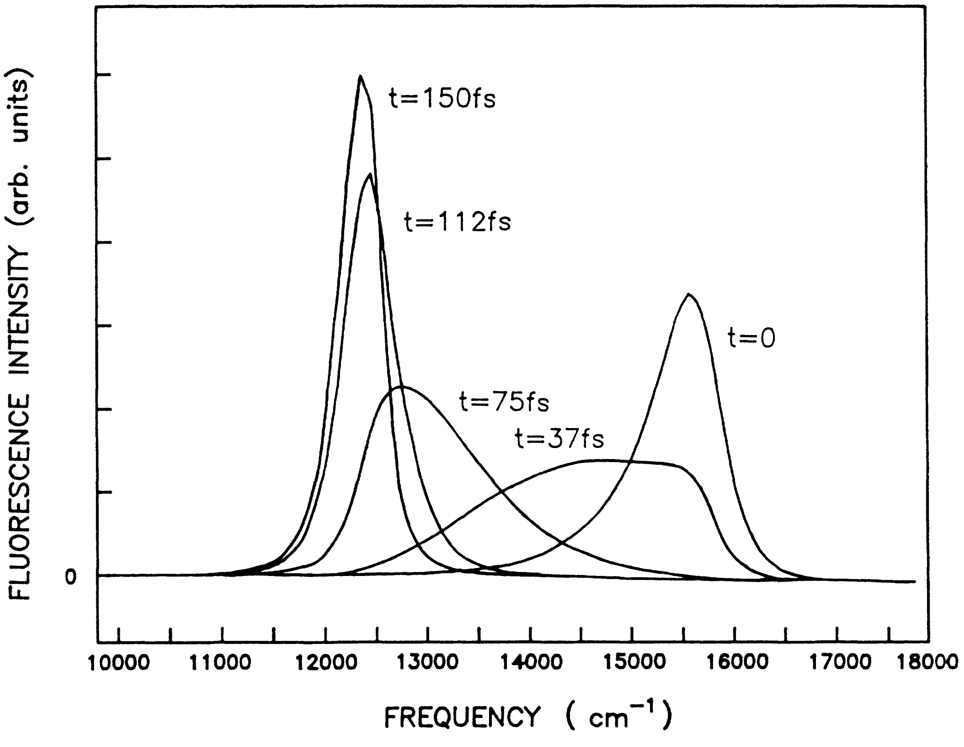

FIG. 2. Time-dependent spectrum of the spontaneously emitted light from an Na_2 molecule following excitation with a short light pulse.

changes in time dramatically. On the other hand, the total fluorescence intensity remains constant in time, consistent with the assumption of the constant value of the transition dipole moment. The spectral width of the observed fluorescence is much larger than the broadening, due to the finite time during which the gate is opened. The spectrum is relatively narrow at $T=0$ and $T=t_{\text{vib}}/2$. At these times the wave packet is close to its turning points, and during the opening of the gate it samples only a small range of difference potential [Fig. 1(b)]. A steeper difference potential at the inner turning point than at the outer turning point (where the wave packet passes through the extremum of this potential) results in a broader spectrum at $T=0$ than at $T=t_{\text{vib}}/2$. At $T=3t_{\text{vib}}/8$ the wave packet reaches its maximum speed, and it moves over a wide range of the difference potential. This produces a much broader spectrum of fluorescence at $T=3t_{\text{vib}}/8$ than at $T=0$, or $T=t_{\text{vib}}$.

Notice that the fluorescence intensity as a function of wavelength is qualitatively the same shape as that of the wave packet as a function of internuclear separation (shown in Fig. 2 of Ref. 2). The distortion arises from the finite temporal and spectral bandwidths inherent in the detection system, and to the nonlinear dependence of the ground-state potential-energy surface on the internuclear coordinate. However, for realistic experimental parameters, it is possible to use the spectrum of the fluorescence to determine approximately the shape of the wave packet during its motion.

In conclusion, we have calculated the time dependence of the spontaneously emitted photons from a coherently excited molecule. We have shown that the spectrum varies significantly in time and provides a useful tool in the studies of coherent phenomena.

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