The Instability of Molecules in Laser Field and Isotope Separation

Ke-hsueh Li
Institute of Physics, Chinese Academy of Sciences

Z. Naturforsch. 36a, 813—818 (1981); received May 11, 1981

In the present paper the nonlinear differential equation describing the selective decomposition of a molecule as an unimolecular reaction has been deduced from the usual time dependent semiclassical Schrödinger Equation. The selective conditions for the instability of a molecule are discussed. The thresholds of the required laser intensities for ICl and HCl diatomic molecules are estimated respectively, where one type of isotope molecules ought to be decomposed for hundred per cent in a laser pulse for different pulse widths. And possibly selective decomposition of the molecule without permanent dipole moment by Raman process is also discussed briefly.

Introduction

The success of the isotope separation for iodine chloride [1] as well as of the excited bimolecular chemical reaction for system HCl + K [2] by lasers has implied that the prevalent theory and conjecture of the isotope separation for polyatomic molecules by lasers [3] might not be seen as general correctly. Because there is no continuum region of energy levels for diatomic molecules to remedy the nonresonance mishap for induced transitions due to the presence of anharmonicity of force constants. But this assumption is just the inevitable presupposition for the theory hitherto. So it comes the problem about the true mechanism of the selective dissociation at least for the diatomic molecules by lasers.

As an unimolecular reaction the dissociation of diatomic molecules without any influence except the laser field is none other than the breaking of the only one chemical bond between two atoms effected by coherent electromagnetic wave. Here we see that the molecular system in the light field may be transforme into an unstable one under certain conditions, while if it is still to remain in a stable state, the chemical reaction does not possible take place. When there is not high nonlinear effect plays a role, the excitation of instability might not be understood. From viewpoint of the microscopic structure of matters the time dependent Hamiltonian describes an open quantum system which does not be approximated by a closed one through perturbation theory in our case. The instability of molecular structure may be described by nonunitary wave functions. Thus the problem for solving the wave functions from Schrödinger Equation is very difficult without perturbation calculation.

In the present paper we want to propose a new theoretical method to describe the selective dissociation of molecules irradiated by lasers on the basis of the semiclassical Schrödinger Equations. So that we remove the obscure conjecture for its microscopic level structures and transition processes. Due to the mathematical difficulty for the evaluation of the wave functions we deduced a macroscopic nonlinear differential equation describing the dynamic behaviours of molecule excited by laser field. Under some reasonable assumptions it can be reduced to a type of inhomogeneous Mathieu Equation may be solved exactly by Floquet Theorem. The unstable Floquet solution gives us the selectivity of molecular dissociation on the laser frequencies. The spectral regions of the selective frequencies will become broader and broader progressively for higher laser powers, and the selectivity breaks down ultimately in accordance with the experiments of the interactions of matters with laser light for high power laser.

We want even more to propose to perform the experiments for the same purpose by using the Raman process according to our results. It is certainly useful for isotope separation of molecules without permanent dipole moments.

Fundamental Equations

We consider the usual time dependent Schrödinger Equation of a molecule in laser light field:

\[ i\hbar \frac{\partial}{\partial t} \psi(t) = H(t) \psi(t), \quad \psi(t+T) = H(t). \] (1)
where \( H(t) \) is the time periodic Hamiltonian:

\[
H(t) = \sum_i \frac{1}{M_i} \Pi_i^2 + \frac{1}{2m} \sum_j \Pi_j^2 + V(t)
\]  

(2)

with

\[
\Pi_i = -i\hbar \nabla_i + \frac{z_i e}{c} A,
\]

\[
\Pi_j = -i\hbar \nabla_j - \frac{e}{c} A
\]

(3a)

the generalized momentum operators of the nuclei and that of the electrons labeled by \( i \) and \( j \) respectively. On the dipole approximation, wave length is much greater than the molecular size, \( A = a \sin \omega_0 t \), \( t \) is the vector potential of the laser field which is related to the field strength by

\[
E = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}.
\]

\[
V = V_{ii'} + V_{ij} + V_{jj'}
\]

and

\[
V_{ii'} = \sum_{ii'} \frac{z_i z_{i'} e^2}{2r_{ii'}}, \quad V_{ij} = -\sum_{ij} \frac{z_i e^2}{r_{ij}},
\]

\[
V_{jj'} = \sum_{jj'} \frac{e^2}{2r_{jj'}}
\]

(3b)

are the contributions to the potential energy arising from nuclear, nuclear-electron, and electronic interactions, respectively. \( \psi(t) \) is the molecular wave-function which can be written as a product of that parts of nuclei and electrons under the Born-Oppenheimer approximation, but it is not necessary in our present case.

Multiply Eq. (1) by \( \psi^\ast(t) \) and from it substract its complex conjugate equation, then follows

\[
i\hbar \left( \frac{\partial}{\partial t} \psi^\ast \psi + \frac{\partial}{\partial t} \psi \psi^\ast \right) = \psi^\ast H \psi - \psi(H \psi)^\ast.
\]  

(4)

Substituting (2) into (4) we obtain the conservation equation of the probability density:

\[
\frac{\partial}{\partial t} \rho + \sum_i \nabla_i J_i + \sum_j \nabla_j J_j = 0,
\]  

(5)

where

\[
\rho = \psi^\ast \psi,
\]

\[
J_i = \frac{1}{2M_i} [\psi^\ast \Pi_i \psi + \psi(\Pi_i \psi)^\ast],
\]

\[
J_j = \frac{1}{2m} [\psi^\ast \Pi_j \psi + \psi(\Pi_j \psi)^\ast]
\]

(6)

are the probability density and the probability current densities for nuclei and electrons respectively. If we multiply Eq. (5) by the coordinate of the kth nucleus from the mass centre as the origin of coordinate and take the space integral, then we obtain:

\[
\frac{d}{dt} \langle r_K \rangle + \sum_i \int r_K \nabla_i J_i \, d\tau = \frac{1}{M_K} \int \psi^\ast \Pi_K \psi \, d\tau = 0.
\]  

(7)

According to the Stokes theorem the first summation is zero except the kth term \( \int r_K \nabla_J J_K \, d\tau = -\int J_K \, d\tau \) and the second summation is always zero, then follows

\[
\frac{d}{dt} \langle r_K \rangle = \int J_K \, d\tau.
\]  

(8)

Because of the Eq. (6) the (8) can be written as

\[
\frac{d}{dt} \langle r_K \rangle - \frac{1}{M_K} \frac{d}{dt} \langle \Pi_K \rangle = 0.
\]  

(9)

Differentiate the Eq. (9) with respect to time once more, we get the eq. of motion of the kth nucleus:

\[
\frac{d^2}{dt^2} \langle r_K \rangle = \frac{1}{M_K} \frac{d}{dt} \langle \Pi_K \rangle = 0.
\]  

(10)

Because of

\[
\frac{d}{dt} \langle \Pi_K \rangle = \left( \frac{\partial}{\partial t} \Pi_K \right) + (i\hbar)^{-1} \langle [\Pi_K, H] \rangle
\]  

(11)

and

\[
\frac{\partial}{\partial t} \Pi_K = \frac{z_K e}{c} \frac{\partial}{\partial t} A = -z_K e E_0 \cos \omega_0 t,
\]

\[
[A, H] = \frac{1}{2M_K} [\Pi_K, \Pi_K^2] + [\Pi_K, V].
\]  

(12)

By the dipole approximation

\[
[A, \Pi_K^2] = 0, \quad [A, V] = -i\hbar \nabla_K V,
\]

\[
\nabla_K V = \sum_i F_{K_i} + \sum_j F_{K_j} = -\sum_i \frac{z_K z_i e^2}{2r_{K_i}^3} + \sum_j \frac{z_K e^2}{r_{Kj}^3}.
\]  

(13)

So that

\[
M_K \frac{d^2}{dt^2} \langle r_K \rangle + \left[ \sum_i F_{K_i} + \sum_j F_{K_j} + z_K e E_0 \cos \omega_0 t \right] = 0.
\]  

(14)
If we consider only the diatomic problem the equation of one of the two atoms is
\[
M_1 \frac{d^2}{dt^2} \langle r_1 \rangle + \left( F_{12} + \sum_j F_{1j} + Z_1 e \ E_0 \ cos \ \omega_0 t \right) = 0 .
\]
From the same method one obtains the same kind dynamic equation of the jth electron:
\[
m \frac{d^2}{dt^2} \langle r_j \rangle + \left( \sum'_F F'_{jj} + \sum_i F_{ij} - e_j E_0 \ cos \ \omega_0 t \right) = 0 ,
\]
where i takes only 1, 2 two values, and e_j = e, the charge of the electron. Because we are interested only in the problem of the motion of a nucleus with its surrounding electrons as a whole body, so we divide the all n electrons into two groups. One of them is that of from j = 1 to j = m, the other from j = m + 1 to j = n. Add all the j = 1, ..., m electron equations (16) to the Eq. (15) of the 1. nucleus, then follows
\[
M_1 \frac{d^2}{dt^2} \langle \vec{r}_1 \rangle + f_1(\langle \vec{r} \rangle) + e^* E_0 \ cos \ \omega_0 t = 0 ,
\]
where
\[
\langle \vec{r}_1 \rangle = \langle r_1 \rangle + \frac{m}{M_1} \sum_{j=1}^m \langle r_j \rangle
\]
is the average position of the composite system. Beware of the difference between \( \langle \vec{r}_1 \rangle \) and \( \langle \vec{r} \rangle \) including also the average position of the composite system of 2. nucleus and its surrounding electrons, and
\[
f_1(\langle \vec{r} \rangle) = \left( F_{12} + \sum_{j=1}^m \sum_{j'=m+1}^n F_{jj'} + \sum_{j'=m+1}^n F_{1j'} + \sum_{j=1}^m F_{2j} \right).
\]
As a stable whole system the attractive force of nucleus 1 to its surrounding electrons \( \sum_{j=1}^m F_{1j} \) is balanced by the repelling forces of such electrons themselves against each other \( \sum_{j'=1}^m \sum_{j''=1}^m F_{jj''} \). The \( f_1(\langle \vec{r} \rangle) \) consists of the repelling force among the nuclei and of that among the surrounding electrons and the attractive forces of the nuclei to the surrounding electrons of the other nuclei. In addition \( e^* = \left( z_1 e - \sum_{j=1}^m e_j \right) \) is the effective charge of 1. nucleus. \( e^* \) depends on the parameters of laser field and the time, since the wave function includes the influence of the laser field. By the same way we obtain the equation of the motion of the nucleus 2 with its surrounding electrons as a whole body against the mass centre:
\[
M_2 \frac{d^2}{dt^2} \langle \vec{r}_2 \rangle + f_2(\langle \vec{r} \rangle) - e^* E_0 \ cos \ \omega_0 t = 0 .
\]
Because of the mass centre at rest it follows that \( f_1 = f_2 = f \). It is easily to put the origins of the coordinate to its position of equilibrium for the Eqs. (17) and (18) respectively. The new coordinates of atoms 1 and 2 are represented by \( u_1 \) and \( u_2 \). Using the relative coordinate \( u_2 - u_1 = u \) one can combine (17) and (18) to one equation
\[
M \frac{d^2}{dt^2} u + f(u) + e^* E_0 \ cos \ \omega_0 t = 0 ,
\]
where \( M \) is the reduced mass \( M = M_1 M_2 / (M_1 + M_2) \). The expansion of \( f(u) \) at the equilibrium position can be made as
\[
f(u) = f' u + f'' u^2 + ....
\]
The term \( f(0) = 0 \) ensures the condition of equilibrium. Pay attention to the relation of the effective charge \( e^* \) with its polarization \( P \):
\[
e^* = - \int_0^\infty d\tau = \frac{1}{4\pi} \int \nabla P \, d\tau = \frac{1}{4\pi} \oint P \, d\sigma .
\]
If the polarization \( P \) is assumed as a cylinder with a cross section \( s \). Then it follows
\[
e^* = (s/2\pi) P .
\]
Expanding \( P \) in a series with respect to the displacement and the external field on the basis of nonlinear optics:
\[
P = (P_0 + \chi' u + \chi'' u^2 + ...)
\]
and substituting (20) — (23) into (19) follows a very complex nonlinear differential equation of parametric excitation. But for the experimental conditions it is satisfactory to keep only the lowest nonlinear terms. So that this equation can be simplified to
\[
M \frac{d^2u}{dt^2} + f' u + f'' u^2 + \frac{s P_0}{2\pi} E_0 \ cos \ \omega_0 t
\]
and
\[
+ \frac{s' P_0}{2\pi} E_0 \ cos \ \omega_0 t + \frac{s'' P_0}{2\pi} E_0^2 \ cos^2 \omega_0 t = 0 .
\]
Selectivity on Laser Frequencies

Before proceeding to discuss the instabilities of the solutions of Eq. (24), we will compare it with that used by Bloembergen [4] to investigate the isotope separation by laser:

\[ X + 0)2 X \sim 7 X = e^* E_0 \cos \omega_0 t. \]

The Joos's solutions [5] which were used by Bloembergen as the solutions to the above equation are only correct for constant effective charge \( e^* \) and without the damping term. But from the above discussion the effective charge can not be held as a constant and obeys the relations (21) and (22). On the other hand before taking the term \( u^3 \) the more important nonlinear terms composed by \( E \) and \( X \) (in our case \( u \) as in expansion (23)) must be taken at first. So we see that the more correct description of the behaviours of a molecule undergoing the laser action is only possible by the Eq. (24) but not by that used by Bloembergen.

When the amplitude of a molecular vibration mode in laser field is not yet great enough to consider the nonlinear term \( u^2 \), so the Eq. (24) degrades to an inhomogeneous Mathieu equation

\[
\frac{d^2 u}{dt^2} + (\lambda + 2 h \cos 2\tau) u = h_1 \cos 2\tau + h_2 \cos^2 2\tau
\]

with

\[
\tau = \frac{1}{2} \omega_0 t, \quad \frac{f'}{M} = \omega^2, \quad \lambda = \frac{4 \omega^2}{\omega_0^2},
\]

\[
h = \frac{s P_0 E_0}{\pi M \omega_0^2}, \quad h_1 = -\frac{2 s P_0 E_0}{\pi M \omega_0^2},
\]

\[
h_2 = -\frac{2 s \chi E_0^2}{\pi M \omega_0^2}.
\]

This equation describes mainly a vibrational process of the coherent parametric excitation rather than a simple forced oscillation. The physical meaning of the Eq. (24) is clear: All the terms including the external field \( E \) are from the polarization expansion (23) induced by laser light. And this polarization (the motion of electron cloud of molecule) modulates or parametric excites further the vibrations of nuclei against each other.

According to Kotowski’s method [6] we know that the solution of (25) consists of the general solutions of homogeneous part of this equation

\[
U_1(\tau) = e^{i\mu \tau} \sum_{n=-\infty}^{\infty} a_n e^{i2\pi n \tau},
\]

\[
U_2(\tau) = e^{-i\mu \tau} \sum_{n=-\infty}^{\infty} a_n e^{-i2\pi n \tau}, \quad (27)
\]

and of the particular solution of the inhomogeneous equation

\[
U_p(\tau) = \frac{U_2(\tau)}{\Delta} \int U_1(t) \eta(t) dt - \frac{U_1(\tau)}{\Delta} \int U_2(t) \eta(t) dt. \quad (28)
\]

Where \( \eta(t) \) is the inhomogeneous term of Eq. (25) and

\[
\Delta = U_1(\tau) U'_2(\tau) - U_2(\tau) U'_1(\tau) = \text{const} \neq 0.
\]

The integral of the particular solution is easily to perform. On the basis of the discussion by Kotowski we know that the particular solution in our case is a time periodic function describing the stable oscillation of the molecule. If the parameters of external field fall on the boundaries of stable and unstable regions of the solutions in Strutt scheme of homogeneous Mathieu equation then the particular solution shall diverge. In this case the instability of the still present unstable parts of solutions on the boundaries is only to some extent to enhance. Therefore the main character of the instability of a solution is determined only by unstable solutions (27) of the homogeneous part of Equation (25). Because the amplitude of a molecule can not decay under the interaction by laser from its no perturbation value, so the unstable solution may only take the following branch:

\[
u(\tau) = u_0 e^{i\mu \tau} \sum_{n=-\infty}^{\infty} a_n e^{i2\pi n \tau}. \quad (29)
\]

Substituting (29) into the left hand side of (25) follows the recursive form of \( a_n \)

\[
a_{\pm,n} = \frac{a_{\pm,(n-1)}}{\lambda + (i 2 n + \mu)^2 - h^2} a_{\pm,(n-1)}.
\]

It is important that the real part of \( \mu \) is different from zero, so the amplitude of molecule grows with time in a laser field. Therefore \( \mu \) is also called as the growth rate, and obeys the relation [7]:

\[
cosh \pi \mu = u(\pi; \lambda, h).
\]

(31)
Under the small field approximation (this is always valid in our case) only by \( \lambda = n^2 (n = 0, 1, 2, \ldots) \) in very narrow regions the \( \mu \) takes real values. On the (26) \( \lambda = 4 \omega^2 / \omega_0^2 \) one obtains

\[
\omega = \frac{1}{2} n \omega_0 \tag{32}
\]

the condition of the selectivity on the laser frequencies due to the instability. Neglecting the case \( \omega_0 > \omega \) (photon energy exceeds the eigenvalue of the molecular vibration) the selective condition (32) represents the states of the dissociation or the chemical reaction of molecules, when the eigen-frequency of a molecule is in resonance with the laser frequency or its integer or half integer sub-harmonics. For \( \omega_0 = \omega \) viz. \( \lambda = 4 \) as an example we can take the Poincare (7) expansion on the right hand side of Eq. (31), if \( 2h/\lambda = \epsilon \ll 1 \), it is satisfied by represent case:

\[
U(\pi; 4, \epsilon) = 1 + 0.171347 \epsilon^4 + \ldots \tag{33}
\]

For the left hand side we may use the very good approximation:

\[
\cos \pi \mu = 1 + \frac{1}{2} (\pi \mu)^2 + \ldots \tag{34}
\]

for the case \( \mu \ll 1 \). So that one can rewrite the Eq. (31) as follows

\[
\frac{1}{2} (\pi \mu)^2 \cong 0.17 \epsilon^4 = 0.17 (2h/\lambda)^4. \tag{35}
\]

Because \( h = s P'_0 / \pi M \omega_0^2 \) we get

\[
E_0 = \frac{\pi \sqrt{\pi \mu M \omega_0^2}}{\sqrt{0.34 s P_0'}} \tag{36}
\]

the relation between the growth rate \( \mu \) and the field strength of the laser light \( E_0 \). If we require the molecules to be irradiated by lasers with resonance frequency and to decompose in laser pulse widths as \( t = 10^{-7}, 10^{-6}, 10^{-5} \) sec for \( 100\% \) respectively, we expect the amplitude to grow about 50 times from its zero point amplitude \( u_0 \) (the zero point amplitude of \( H_2 \) is a few tenths of its distance in equilibrium). So that from (29) follows

\[
e^{\mu t} = \rho^u (\omega_0^2/2 \mu t) \cong 50 \tag{37}
\]

and

\[
\mu \cong 2 \ln 50 / \omega_0 \Delta t. \tag{38}
\]

The effective charge of HCl is \( e^* = 0.76 \) e, the distance between the two atoms at equilibrium is \( r_0 = 1.2746 \) Å, the eigenfrequency \( \omega = 5.44 \times 10^{14} \) sec\(^{-1} \), and reduced mass \( \bar{M} = 1.62 \times 10^{-24} \) g, we estimate

\[
s P'_0 \cong 1.43 \times 10^{-2}. \tag{39}
\]

Substituting Eqs. (37) – (39) into (36) we obtain the thresholds of lasers for different pulse widths \( \Delta t \) in Table 1.

For the diatomic molecule ICl we have the estimated bondlength about \( 2.3 \) Å, reduced mass \( \bar{M} = 4.6 \times 10^{-23} \) g, effective charge \( e^* = 0.52 \) e [8], eigen-frequency of one type of isotope ICl \( \omega = 7.2 \times 10^{13} \) sec\(^{-1} \), which is bit greater than that of the other type about \( 8 \) cm\(^{-1} \). So we have obtained the threshold values for the same conditions as above also given in Table 1.

<table>
<thead>
<tr>
<th>( \Delta t ) (sec)</th>
<th>HCl</th>
<th>ICl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_0 ) (V/cm)</td>
<td>( P_0 ) (W/cm(^2))</td>
<td>( E_0 ) (V/cm)</td>
</tr>
<tr>
<td>( 10^{-7} )</td>
<td>1.9 \times 10^5</td>
<td>8.8 \times 10^7</td>
</tr>
<tr>
<td>( 10^{-6} )</td>
<td>4.9 \times 10^4</td>
<td>6 \times 10^6</td>
</tr>
<tr>
<td>( 10^{-5} )</td>
<td>1.9 \times 10^4</td>
<td>8.8 \times 10^6</td>
</tr>
</tbody>
</table>

According to the results here we suggest to perform the experiments for diatomic molecules to test the present theory with longer pulse widths of lasers. The dependence of the threshold of laser field strength for molecular dissociation on the pulse width \( \Delta t \) is the main character of the parametric excitation. It is worth to note that we have not considered the damping effect in the dynamic equation above. And the damping term can certainly correct the results for longer laser pulse widths. For c.w. laser it is just this correction to decide the threshold of laser field strength.

**Discussion**

In the above equation we have neglected the term \( u^2 \) in the Eq. (24), that is equivalent to disregard the dependence of force constant on the amplitude of vibrational mode. This is not correct naturally for great amplitude oscillation corresponding to higher excited states. It is difficult to solve the nonlinear differential equation, nevertheless one can give the conditions of instabilities of it as follows:

Our purpose is to discuss the selective decomposition of molecules in laser field. But any decomposition i.e. the unstable no periodic oscillation must be rising from the first initial instability of its amplitude permitting to neglect the anharmonicity of its
force constant. The condition of instabilities in this step have be discussed in the last section. But the first instability of Mathieu equation ensures by no means the instability for the solutions of the nonlinear Mathieu equation. In contrast it is shown by Hsieh [9] that in the linearly unstable region of the \((\lambda, h)\) parameter space nonlinear stable solutions can be found, in spite of the fact that one can not answer the question whether and how an initial disturbance will evolve into these asymptotic solutions.

Let us assume \(u = u_0 e^{-\lambda t}\) is a stable, time periodic solution satisfying the nonlinear Equation (24). So that one demands to ask about the conditions may be satisfied by this solution when it falls on the unstable region. To this end we consider the equation satisfying by the small increament of it to its neighbouring solution. Assuming \(u_1 = u + \Delta u\) is that neighboring solution, substituting it into the Eq. (24) so follows

\[
M \frac{d^2}{dt^2} \Delta u + f' \Delta u + 2 f'' u \Delta u + \frac{s P_0'}{2\pi} \Delta u E_0 \cos \omega_0 t = 0,
\]

(40)

where the term \((\Delta u)^2\) is neglected. Introducing the new variable \(\tau = (\omega_0/2) t\), \(x = \Delta u\) and taking only the real part of \(u\), it gives the Hill equation of well know type:

\[
\frac{d^2x}{d\tau^2} + \frac{4}{\omega_0^2 M} \left( f' + 2 f'' u_0 \cos \Omega t + \frac{s P_0'}{2\pi} E_0 \cos 2\tau \right) x = 0.
\]

(41)

Herein it is to consider that the value of frequency \(\Omega\) is restricted by the Eq. (25), whose unstable solutions oscillate with frequencies of multiple \(\omega_0\) except an exponential factor with real \(\mu\) values (27). So that the Hill equation has the standard form:

\[
\frac{d^2x}{d\tau^2} + \left[ \lambda + \Gamma \phi(\tau) \right] x = 0
\]

(42)

discussed by Strutt [10]. Where \(\phi(\tau)\) is a limited, differentiable and real periodic function with period \(2\pi\). The conditions for unstable solutions had been given by Strutt [10]. For our case it is in coincidence with the expression (32). This fact implies that if a solution is unstable in its first initial stage, so that also may be unstable in the stage of its nonlinear evolution at least for the case to remain the nonlinear term \(u^2\).

In the present paper it implies an assumption that except the molecules to dissociate by laser there are no other things in presence. So that the dissociation of molecule does signify the completely flying away of two atoms from each other. In the fact the chemical reaction may occure perhaps in the high vibrational excited states, if an other type of molecules participating in chemical reaction in presence. But the unstable excitation is indeed the inevitable mechanism for all cases.

The more rigorous treatment of a diatomic molecular problem here in the present paper may be extended to the normal modes of polyatomic molecules. So that the theory of the selective dissociation of a molecule by laser should be unified on the basis of elementary process described by Schroedinger equation. And we see that the instability of a molecule irradiated by laser light is a high nonlinear phenomenon of parametric excitation. But under small amplitude approximation as above treated one can always get a good understanding of the dissociation mechanism.

For the molecule without the permanent dipole, e.g. \(H_2, O_2, N_2,\) etc., substitute the Eq. (23) into (19) neglecting the terms from the permanent dipole follows the similar equation of the coherent parametric excitation. So that no matter the molecule has a permanent dipole moment or not, the laser light can always stimulate it to unstable vibration and even to dissociate it, but through either infrared or Raman process.