Laser-pulse requirements for coherent and mode-selective excitation in the quasicontinuum of polyatomic molecules

Eli Yablonovitch

Pierce Hall, Harvard University, Cambridge, Massachusetts 02138
Received May 27, 1977

We show that the theory of nuclear magnetic relaxation applies with equal validity to intramolecular relaxation in the quasicontinuum of polyatomic molecules. This theory permits an analysis of the laser-pulse requirements for vibrational-mode selectivity and coherent multiphoton excitation. The laser Rabi precession frequency, $\mu\mathcal{E}/\hbar$, should exceed $1/T_1$ or $1/T_2$, the intramolecular relaxation rates in the quasicontinuum. In practice this requires either an ultra-fast optical-pulse risetime or a slower pulse that is tuned far to the red side of the transition.

Multiphoton-induced unimolecular reactions, such as dissociation[1] and isomerization,[2] have been produced by pulsed high-power infrared lasers. Although isotopic selectivity[3] provoked the initial interest in this process, attention is now directed to the more-general possibilities of multiphoton-induced chemistry.

Within a few thousand wavenumbers of the ground state, the discrete vibrational levels merge into a quasicontinuum[4] which plays a key role in multiphoton-induced chemistry.[5,6] Consider the following approach: Divide the internal molecular degrees of freedom into two groups, the system and the heat bath. Let the driven infrared-active vibrational mode be regarded as the system with Hamiltonian $H_s(x)$. Let the other n vibrational modes in the molecule be the heat bath with Hamiltonian $H(y_1 \ldots y_n)$. The system and the heat bath are coupled by anharmonic terms in the molecular potential described by $V(x,y_1 \ldots y_n)$. The total vibrational Hamiltonian is

$$H = H_s(x) + V(x,y_1 \ldots y_n) + H(y_1 \ldots y_n), \quad (1)$$

where x and y_i represent the phase space coordinates of the system and the heat bath, respectively. The heat bath damping problem described by Hamiltonian Eq. (1) has been thoroughly studied in connection with nuclear magnetic relaxation.[7] We will find that many of those results carry over to the domain of intramolecular relaxation. For simplicity, we will use a semiclassical approach—a quantum description of the system, but a classical description of the heat bath. A fully quantum-mechanical approach, while more correct, gives similar results.[7,8]

The equation of motion for the system density matrix $\rho_{ss'}$ is solved to first and second order in the anharmonic potential $V(x,y_1 \ldots y_n)$. The first-order solution merely renormalizes the energy levels of the system:

$$\Delta E_s = \overline{\langle s | V(t) | s \rangle}, \quad (2)$$

where $V(t)$ depends on time through the classical heat bath coordinates, $V(t) \equiv V[x,y_1(t), \ldots ,y_n(t)]$, and ——— represents statistical averaging over the phase space of the heat bath.

The second-order solution leads to the usual T_1 and T_2 damping terms in the density-matrix equation of motion. Transitions induced by the heat bath between the states s and s' are given[8] by: $\left(\dfrac{1}{T_1}\right)_{ss'} = \dfrac{1}{\hbar^2} \displaystyle\int_{-\infty}^{\infty}$

$$\times \; \overline{\langle s | V(t) | s' \rangle \langle s' | V(t - \tau) | s \rangle} \; \exp(-i\omega_{ss'}\tau)\mathrm{d}\tau. \quad (3)$$

The adiabatic contribution to the damping of the off-diagonal matrix element $\rho_{ss'}$ is given by:

$$\left(\frac{1}{T_2}\right)_{ss'}^{\text{ad}} = \int_0^\infty \overline{\delta\omega_{ss'}(t)\delta\omega_{ss'}(t - \tau)}\mathrm{d}\tau, \quad (4)$$

where $\hbar\delta\omega_{ss'}(t) \equiv \langle s | V(t) | s \rangle - \langle s' | V(t) | s' \rangle$.

Equations (3) and (4) are carried over directly from the theory of nuclear magnetic relaxation.[7] The important question is whether intramolecular relaxation fulfills the validity requirements for the approximations leading to Eqs. (3) and (4). The most important restriction is that the autocorrelation time τ_c of the heat bath should be very short in relation to the strength of the anharmonic potential V:

$$\overline{V^2}\tau_c{}^2/\hbar^2 \ll 1. \quad (5)$$

This can be confirmed as follows: The anharmonic potential $V(x,y_1 \ldots y_n)$ at $t = 0$ is, in general, a function of the vector of heat bath coordinates $[y_i(0)] \equiv [y_1(0), \ldots ,y_n(0)]$. After a time τ of the order of one vibrational period, the heat bath coordinates will have changed to $[y_i(\tau)]$. Assuming that the heat bath vibrational modes are *not completely degenerate*, the vector $[y_i(\tau)]$ will be uncorrelated with $[y_i(0)]$. Therefore, the autocorrelation time is the reciprocal of the frequency spread of heat bath vibrational modes, or typically about a vibrational period, $\tau_c \sim 1/\omega_0$.

In real molecules the anharmonic potential tends to be much smaller than the vibrational quantum $(\overline{V^2})^{1/2} \ll \hbar\omega_0$, even when there is substantial thermal energy in the bath.[9] Therefore, the restriction of Eq. (5) is fulfilled and, in addition, the damping rates $\sim\overline{V^2}\tau_c/\hbar^2$ are much slower than ω_0.

In the full quantum theory of damping,[7] there is a second important requirement that must be satisfied:

$$\hbar \, (\mathrm{d}N/\mathrm{d}E) \gg \hbar^2/\overline{V^2}\tau_c, \quad (6)$$

where $\mathrm{d}N/\mathrm{d}E$ is the heat bath density of states and $\hbar^2/\overline{V^2}\tau_c$ is a typical damping time constant. In a polyatomic molecule, the density of states rises rapidly with increasing energy, so that Eq. (6) may already be satisfied with only $\approx 3000 \; \mathrm{cm}^{-1}$ in the heat bath. [It can
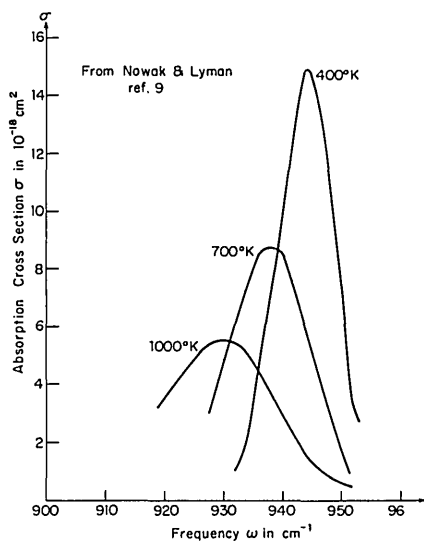
Fig. 1.   The absorption spectrum as a function of temperature in the ν_3 band of SF_6.   Notice the shift to longer wavelengths as temperature is raised.   The linewidth remains fairly narrow at 1000 K, even though the molecule is thermally excited ≈ 9000 cm^{-1} up into the quasicontinuum.

be shown that the inequalities in Eqs. (5) and (6) are equivalent to the two that are needed in deriving Fermi's Golden Rule.[10]]

As an example of the validity of these concepts in a real molecule, Fig. 1 shows the ν_3 absorption band of SF_6 for three different temperatures as heated in a shock tube.[9]   At 1000 K, the spectrum is anharmonically downshifted about 20 cm^{-1} and broadened to a width $\Delta\omega \approx 20$ cm^{-1}.   The heat bath contains about 9000 cm^{-1} of thermal energy at 1000 K, guaranteeing that Eq. (6) is satisfied, i.e., that the molecule is in the quasicontinuum of levels.

The finite linewidth $\Delta\omega$ is caused by a number of contributing mechanisms.   In addition to the intramolecular damping rates $1/T_1$ and $1/T_2$, the rotational structure makes a contribution that we have been ignoring.   Also, there is a special type of inhomogeneous broadening associated with the differences in thermal energy of different members of the canonical ensemble.   These energy fluctuations, $(\overline{\Delta U})^2 = n(kT)^2$, are significant because of the very small size of the intramolecular heat bath.   Molecules with different thermal energies have different mean anharmonic shifts ΔE_s, as given by Eq. (2), thus leading to inhomogeneous broadening.[11]

The important point is that the finite linewidth $\Delta\omega$ places an upper limit on the damping rates $1/T_1$ and $1/T_2$.   Therefore, $1/T_2 < \Delta\omega \simeq 0.02\omega_0$ and the inequality of Eq. (5) is easily satisfied.   Since Eqs. (5) and (6) are both fulfilled, we have established that heat bath damping theory describes intramolecular relaxation in polyatomic molecules.

We will now employ these concepts to address the question of coherence and mode selectivity in multiphoton excitation.   The system equation of motion has been reduced[7] to:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}(H_s,\rho) + \text{damping terms.} \qquad (7)$$

To this must be added the light-wave-induced interaction,

$$H'_{s,s+1} = \sqrt{s+1}\mu\mathscr{E}\,\exp(i\omega t), \qquad (8)$$

where s is the vibrational quantum number of the system, μ is the dipole moment[12] of the transition, $\mathscr{E}$ is the peak electric field of the light wave, and ω is its frequency.   The limit of coherent[13] multiple-photon excitation is specified by

$$\sqrt{s}\,\frac{\mu\mathscr{E}}{\hbar} > \sqrt{\frac{1}{T_2^2} + (\omega - \omega_0)^2}. \qquad (9)$$

In the opposite limit, the off-diagonal elements of the density matrix are $\ll 1$, and Eqs. (7) and (8) reduce to a set of diagonal rate equations.   The up-transition rate is $2\pi(s+1)\omega_R{}^2 g(\omega)$, whereas the down-transition rate is $2\pi s\omega_R{}^2 g(\omega)$, where $\omega_R = \mu\mathscr{E}/\hbar$, the Rabi precession frequency, and $\pi g(\omega) = T_2/[1 + (\omega - \omega_0)^2 T_2^2]$, the standard Lorentzian line shape.

There has been great interest among chemists in vibrational mode selectivity,[15] namely, the excitation of the system degree of freedom to a high energy with a minimum of thermalization to the heat bath.   It is required that the rate of heating significantly exceed the rate of energy relaxation:

$$2\pi s\omega_R{}^2 g(\omega) \gg 1/T_1. \qquad (10)$$

Since T_2 is always $< T_1$, vibrational-mode selectivity is a less stringent condition than fully coherent excitation.   In spite of this, neither condition is easy to achieve.   Both depend on a large Rabi precession frequency to overcome not only the damping rates $1/T_1$ and $1/T_2$, but also the frequency mismatch $(\omega - \omega_0)$ that develops as a result of anharmonicity.   A superficial way to accomplish this is to focus the laser beam more tightly, raising $\mu\mathscr{E}$.   The following reasoning shows why this approach fails:

Consider the laser-pulse intensity I as a function of time, as graphed in Fig. 2.   The peak intensity is chosen to satisfy the condition of Eq. (10).   During the rising portion of the laser pulse, before it has reached its peak intensity, Eq. (10) is not satisfied, and efficient thermalization is taking place.   The energy absorbed by the molecule during the initial cross-hatched portion of the pulse is statistically distributed among all vibrational modes.   If a reaction temperature T_0 is reached during the pulse risetime t_r, then a statistical reaction[5,15] will occur before the conditions for vibrational-mode selectivity have been achieved.   It is necessary to reduce the area of the cross-hatched region in Fig. 2 to ensure a minimum of absorbed thermal energy nKT before the
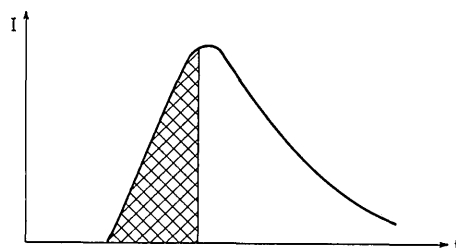

Fig. 2.   A schematic graph of intensity I versus time for a laser pulse.   The area of the cross-hatched portion of the pulse represents an energy fluence (J/cm^2).   The molecular temperature rise depends only on fluence, as specified by Eq. (11).   It should be kept as small as possible to prevent premature nonselective chemical reaction.
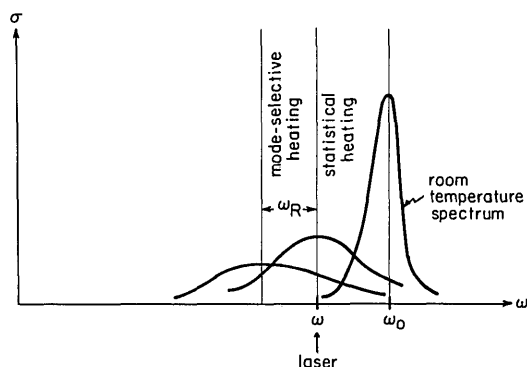
Fig. 3. An illustration of the technique for achieving vibrational-mode selectivity. Ordinary statistical heating shifts the transition into resonance with the laser frequency ω. On resonance, Eq. (10) is satisfied and the heating becomes mode selective until the additional anharmonic shift once again exceeds ω_R, the Rabi precession frequency.

laser peak:

$$T = \frac{1}{nK} \int_0^{t_r} I\sigma \, dt \ll T_0, \tag{11}$$

where σ is the absorption cross section per molecule and n the number of normal modes.

Vibrational-mode selectivity requires that both Eqs. (10) and (11) be satisfied. The peak intensity I must be high enough for Eq. (10), but the product $I \times t_r$ must be low enough for Eq. (11). The crucial constraint is that the rise time be very short. Obviously, a rise time as short as T_2 itself would be quite sufficient. Technologically, this is difficult to achieve, since T_2 is certainly in the picosecond range.

The following technique would help permit the use of a slower pulse while still satisfying Eqs. (10) and (11). The laser could be tuned far to the red side of the transition. The off-resonant absorption[16,17] would be very weak, helping to satisfy Eq. (11). Furthermore, as the molecule heats up, the anharmonic shift would tend to reduce the frequency mismatch $\omega_0 - \omega$ to zero just at the moment when the laser pulse is near its peak. This, in turn, would help to satisfy Eq. (10). A schematic illustration of the process is shown in Fig. 3.

A numerical example would be helpful. Suppose it were desired to achieve a dipole matrix element in SF_6 of $\mu \mathcal{E} \sim 15$ cm^{-1} while keeping the random thermal heating below $T = 1000$ K. This dipole matrix element[12] requires a peak intensity of $I \sim 10^{10}$ W/cm^2. Assuming that the laser pulse is a linear ramp, the maximum permissible rise time is

$$t_r = (2nKT)/I\sigma, \tag{12}$$

where we have made the rough assumption that σ is constant. For large detuning, $\omega_0 - \omega \sim 40$ cm^{-1}, the absorption cross section[17] is small, $\sigma \sim 10^{-19}$ cm^2. Under these conditions, $t_r \lesssim 300$ psec would be fast enough to fulfill the conditions of Eqs. (10) and (11) for vibrational-mode selectivity. Such fast-rising pulses can be generated by optical free induction decay.[18]

As the molecule heats up, it is shifted into resonance with the laser, bringing it into the regime where Eq. (10) is satisfied. Further energy deposition is of a vibrationally mode-selective character or possibly even of a coherent nature. Nevertheless, the extent of additional mode-selective heating is severely limited by the an-harmonicity associated with it. The resonance continues to shift to longer wavelengths until the additional anharmonicity overwhelms Eq. (10).

The anharmonic shift is, to a good approximation, proportional to the total energy in the molecule.[19] Let A be the constant of proportionality. As the resonance shifts from ω_0 to ω, the energy deposited is $nKT = (\omega_0 - \omega)/A$, going primarily into heat bath modes. Then there is mode-selective energy deposition U, until the additional anharmonic shift becomes comparable to the Rabi precession frequency ω_R. Thus the maximum selectively deposited energy is $U = \omega_R/A$. Clearly, the magnitudes of $\omega_0 - \omega$ and ω_R determine the temperature, the energy in the reaction coordinate, and whether a mode-selective chemical reaction will occur.

References

1. N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. 18, 225 (1971).
2. A. Yogev and R. M. J. Benmair (to be published).
3. R. V. Ambartzumian, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Pis'ma Zh. Eksp. Teor. Fiz. 20, 597 (1974) [JETP Lett. 20, 273 (1974)]; J. L. Lyman, R. J. Jensen, J. Rink, C. P. Robinson, and S. O. Rockwood, Appl. Phys. Lett. 27, 87 (1975).
4. S. Mukamel and J. Jortner, J. Chem. Phys. 65, 5204 (1976).
5. J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. 38, 1131 (1977).
6. P. Kolodner, C. Winterfeld, and E. Yablonovitch, Opt. Commun. 20, 119 (1977).
7. F. Bloch, Phys. Rev. 105, 1206 (1957). A. G. Redfield, in Advances in Magnetic Resonance, J. S. Waugh, ed. (Academic, New York, 1965), Vol. 1.
8. Equation (3) is actually correct only in the limit of high heat bath temperature. In general, the quantum mechanical form of Eq. (3) should be used. See Ref. 7.
9. A. V. Nowak and J. L. Lyman, J. Quant. Spectros. Radiat. Transfer 15, 945 (1975).
10. R. H. Pantell and H. E. Puthoff, Fundamentals of Quantum Electronics (Wiley, New York, 1969).
11. Since the molecules are assumed to be isolated, the correlation times for energy changes is infinite and microcanonical averaging should be used in Eq. (2). Then the full canonical ensemble will yield an inhomogeneous distribution of energy shifts ΔE_s.
12. P. N. Schatz and D. F. Hornig, J. Chem. Phys. 21, 1516 (1953).
13. R. J. Glauber, Phys. Rev. 130, 2529, and 131, 2766 (1963).
14. D. F. Dever and E. Grunwald, J. Am. Chem. Soc. 98, 5055 (1976).
15. E. R. Grant, M. J. Coggiola, Y. T. Lee, P. A. Schulz, and Y. R. Shen (to be published).
16. R. T. Lageman and E. A. Jones, J. Chem. Phys. 19, 534 (1951).
17. R. V. Ambartzumian, N. P. Fuzikov, Yu. A. Gorokhov, V. S. Letokhov, G. N. Marakhov, and A. A. Puretzky, Opt. Commun. 18, 517 (1976).
18. E. Yablonovitch and J. Goldhar, Appl. Phys. Lett. 25, 580 (1974); H. S. Kwok and E. Yablonovitch, Appl. Phys. Lett. 30, 158 (1977).
19. R. S. McDowell, J. P. Aldridge, and R. F. Holland, J. Phys. Chem. 80, 1203 (1976).
20. S. Mukamel (to be published).