Transient Experiments and Relaxation Processes Involving Rotational States

W. H. Flygare* and Thomas G. Schmalz

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801

Transient experiments on molecular rotation levels in gas-phase microwave spectroscopy have developed rapidly in the past few years, and we now have a sufficiently sound understanding of the phenomena involved to justify a short review and comparison with the better known transient experiments in nuclear magnetic resonance. Although isolated reports of observed microwave transient effects appear earlier in the literature,[1-4] the recent development of faster electronic measuring methods has led to a great deal of current interest.[5-19]

Transient experiments normally involve observing the effects of bringing an ensemble of two-level quantum mechanical systems into or out of resonance with high-power radiation in times short relative to the relaxation processes in the two-level system. Of course, transient experiments in magnetic resonance have been familiar for two decades. Normally, the relaxation times in magnetic resonance experiments are 10^6–10^7 times longer than in gas-phase rotational systems. Thus, the radiation switching and speed of detection requirements in rotational state spectroscopy are much more severe, and this has led, in part, to the long delay in developing transient experiments in rotational microwave spectroscopy.

Transient experiments on rotation states are broadly classed as those involving coherent absorption and coherent spontaneous emission. These phenomena are

most clearly defined in the limits where the radiation frequency is either within or outside of the steady-state line width (including power saturation) of a two-level transition. We will simplify our discussion to the normal case of negligible Doppler broadening in the steady-state rotational transition. *On-resonance* refers to the condition where the external radiation frequency is within the line width of the steady-state transition. *Off-resonance* refers to the condition where the radiation frequency is outside of the line width of the steady-state transition. In these limiting regions *transient absorption* usually occurs immediately after the radiation has changed from the off-resonance to the on-resonance condition. *Transient emission* usually occurs immediately after the radiation has changed

W. H. Flygare received his A.B. degree from St. Olaf College in Northfield, Minn., and the Ph.D. from the University of California, Berkeley (in 1961). He then joined the faculty of the University of Illinois, where he is Professor of Chemistry. Dr. Flygare's research interests include the theoretical aspects of molecular structure, the experimental and theoretical study of electric and magnetic interactions in molecules, vibrational and rotational relaxation phenomena, microwave conductivity measurements in solids, light scattering in pure liquids and in solutions of biologically interesting molecules, and the structure of liquids.

Thomas G. Schmalz was born in Springfield, Ill., studied at Montana State University for his B.S. degree, and received the Ph.D. from the University of Illinois in 1975. He is now at The James Franck Institute, University of Chicago. Dr. Schmalz's research interests are in the magnetic properties of small molecules, gas-phase collisional interactions, and atomic and molecular scattering.

(1) R. H. Dicke and R. H. Romer, *Rev. Sci. Instrum.*, 26, 915 (1955).
(2) M. L. Unland and W. H. Flygare, *J. Chem. Phys.*, 45, 2421 (1966).
(3) R. M. Hill, D. E. Kaplan, G. F. Herman, and S. K. Ichiki, *Phys. Rev. Lett.*, 18, 105 (1967).
(4) H. Harrington, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1968.
(5) J. M. Levy, J. H. S. Wang, S. G. Kukolich, and J. I. Steinfeld, *Phys. Rev. Lett.*, 29, 395 (1972).
(6) B. Macke and P. Glorieux, *Chem. Phys. Lett.*, 14, 85 (1972); 18, 91 (1973); *Chem. Phys.*, 4, 120 (1974).
(7) J. H. S. Wang, J. M. Levy, S. G. Kukolich, and J. I. Steinfeld, *Chem. Phys.*, 1, 141 (1973).
(8) A. H. Brittain, P. J. Manor, and R. H. Schwendeman, *J. Chem. Phys.*, 58, 5735 (1973).
(9) T. Amano and T. Shimizu, *J. Phys. Soc. Jpn.*, 35, 237 (1973).
(10) J. C. McGurk, R. T. Hofmann, and W. H. Flygare, *J. Chem. Phys.*, 60, 2922 (1974).
(11) J. C. McGurk, T. G. Schmalz, and W. H. Flygare, *J. Chem. Phys.*, 60, 4181 (1974).
(12) S. R. Brown, *J. Chem. Phys.*, 60, 1722 (1974).
(13) T. L. Weatherly, Q. Williams, and F. Tsai, *J. Chem. Phys.*, 61, 2925 (1974).
(14) J. C. McGurk, H. Mäder, R. T. Hofmann, T. G. Schmalz, and W. H. Flygare, *J. Chem. Phys.*, 61, 3759 (1974).
(15) G. M. Dobbs, R. H. Michaels, J. I. Steinfeld, J. H. S. Wang, and J. M. Levy, *J. Chem. Phys.*, 63, 1904 (1975).
(16) H. Mäder, J. Ekkers, W. Hoke, and W. H. Flygare, *J. Chem. Phys.*, 63, 4380 (1975).
(17) W. E. Hoke, J. Ekkers, and W. H. Flygare, *J. Chem. Phys.*, 63, 4075 (1975).
(18) R. M. Somers, T. O. Poehler, and P. E. Wagner, *Rev. Sci. Instrum.*, 46, 719 (1975).
(19) S. L. Coy, *J. Chem. Phys.*, 63, 5145 (1975).

from the on-resonance to the off-resonance condition. In magnetic resonance, the term transient nutation is used to describe transient absorption and free induction decay is used to describe spontaneous coherent transient emission. We will attempt to compare the phenomena here. In the more complicated case where the radiation frequency is changed between two different points within the line width, the concepts of absorption and emission become less meaningful. However, in the limits described above, the descriptions are appropriate.

Basic Theory and Experiment

We will review briefly the theory of the interaction of classical coherent electromagnetic radiation with a two-level quantum system through the electric dipole interaction in the limit where the pressure broadening is large relative to Doppler shifts. The complete theory, including the Doppler effects, is given elsewhere.[20]

The radiation electric field represented by the plane-polarized traveling wave (along the z axis)

$$E(t) = 2\epsilon \cos(\omega t - kz) \qquad (1)$$

induces a macroscopic dipole moment or polarization in an ensemble of two-level systems which we write in the form

$$P = (P_r + iP_i)e^{i(\omega t - kz)} + cc \qquad (2)$$

where cc is the complex conjugate. The time dependence of the real and imaginary components of the polarization per unit volume, P_r and P_i, together with the two-level population difference per unit volume, ΔN, is determined by the three coupled differential equations[20]

$$\frac{dP_r}{dt} + \Delta\omega P_i + \frac{P_r}{T_2} = 0$$

$$\frac{dP_i}{dt} - \Delta\omega P_r + \varkappa^2\epsilon\left(\frac{\hbar\Delta N}{4}\right) + \frac{P_i}{T_2} = 0$$

$$\frac{d}{dt}\left(\frac{\hbar\Delta N}{4}\right) - \epsilon P_i + \frac{\hbar}{4}\frac{(\Delta N - \Delta N_0)}{T_1} = 0 \qquad (3)$$

$$\Delta\omega = \omega_0 - \omega$$

$$\varkappa = \frac{2}{\hbar}|\langle a|\mu|b\rangle|$$

Here ω_0 is the molecular transition frequency, ω is the frequency of the radiation, μ is the electric dipole moment operator, and a and b denote the lower and upper levels, respectively. Collisions between the molecules have been taken into account in eq 3 by assuming that, when the radiation is switched off ($\epsilon = 0$), P_r and P_i decay to their equilibrium value of zero with the relaxation time T_2 while ΔN decays to its equilibrium value of ΔN_0 with the relaxation time T_1. Equations 3 are analogous to the Bloch equations which describe the interaction of coherent electromagnetic radiation with a two-level spin ½ system in a constant magnetic field through the magnetic dipole interaction.[21] They are thus capable of describing transient effects in nuclear magnetic resonance (NMR) and electron spin resonance (ESR) as well as rotational and vibrational spectros-

copy. All the phenomena observed in the electric resonance case have their analogs in the magnetic resonance case. Equations 3, when properly modified to include Doppler effects, are also capable of describing transient phenomena in infrared spectroscopy. The analogs of many of the transient phenomena discussed here have recently been observed in the infrared region,[22-24] but this work is beyond the scope of the present paper.

In NMR T_1 is called the longitudinal or spin–lattice relaxation time.[25] It represents the inverse of the rate at which energy is exchanged between the spin system and the surroundings. Since in microwave rotational experiments energy is stored in the form of a population difference, T_1^{-1} is also the rate at which this stored energy is released to the surroundings. T_2 in NMR is called the transverse or spin–spin relaxation time.[25] It represents the rate at which the individual spins lose coherence. Very often in NMR the apparent T_2 contains a significant contribution from inhomogeneity in the magnetic field. If each spin feels a slightly different field at its local position, it will evolve in time slightly differently, leading to a loss of coherence. Many of the pulse methods developed in NMR are an attempt to overcome inhomogeneous broadening.[26] The analogue of inhomogeneous broadening in microwave spectroscopy is Doppler broadening, where the interaction of the field with each dipole is slightly different depending on its local velocity. In the experiments discussed here Doppler broadening is usually negligible, so that T_2 can be interpreted as a loss of coherent polarization due to molecular interactions. Of course, field inhomogeneity in the electric dipole case can be produced by applying an inhomogeneous electric field to the sample.

In normal microwave spectroscopy the frequency of the incident oscillator is swept through the resonance line width in a period of time long relative to the relaxation processes. It is easy to show that the absorption coefficient, γ, is then related to the imaginary part of the polarization by the equation

$$\gamma = -\frac{4\pi\omega}{c}\frac{P_i}{\epsilon} \qquad (4)$$

Equations 3 can be solved in steady state where $dP_r/dt = dP_i/dt = d\Delta N/dt = 0$ for P_i to give the absorption coefficient of

$$\gamma(\omega) = \frac{\left(\frac{4\pi\omega}{c}\right)\left(\frac{\hbar\varkappa^2\Delta N_0}{4}\right)(1/T_2)}{(1/T_2)^2 + (\Delta\omega)^2 + (T_1/T_2)\varkappa^2\epsilon^2} \qquad (5)$$

$\gamma(\omega)$ in eq 5 gives the normal Lorentzian line shape with the half-width at half-height given by

$$\Delta\nu_{1/2} = \Omega_p/2\pi = \frac{1}{2\pi}[(1/T_2)^2 + (T_1/T_2)\varkappa^2\epsilon^2]^{1/2} \qquad (6)$$

where $\Omega_p/2\pi$ indicates the power-saturated line width. If low power radiation is used, $(1/T_2)^2 \gg (T_1/T_2)\varkappa^2\epsilon^2$, and the normal half-width at half-height of the Lo-

(20) J. C. McGurk, T. G. Schmalz, and W. H. Flygare, *Adv. Chem. Phys.*, **25**, 1 (1974).

(21) F. Bloch, *Phys. Rev.*, **70**, 460 (1946).

(22) B. Hocker and E. L. Tang, *Phys. Rev.*, **184**, 356 (1969).

(23) R. G. Brewer and R. L. Shoemaker, *Phys. Rev. Lett.*, **27**, 631 (1971); **28**, 1430 (1972); *Phys. Rev. [Sect.] A*, **6**, 2001 (1972).

(24) M. T. Loy, *Phys. Rev. Lett.*, **32**, 814 (1974).

(25) See, for instance, the description in J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959.

(26) See, for instance, T. E. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971.
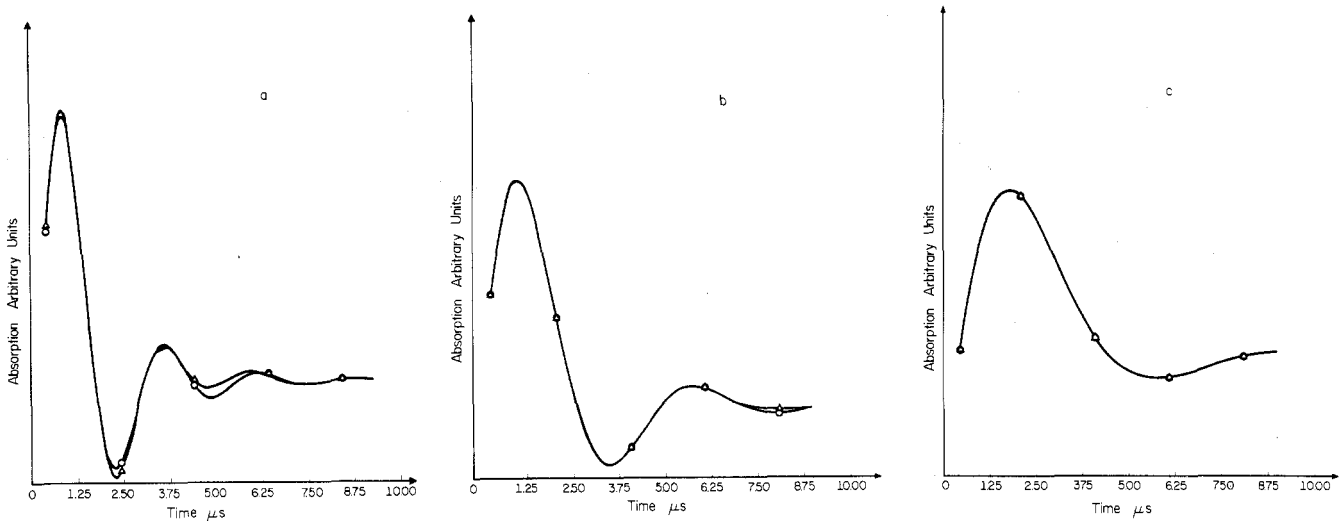
Figure 1. Comparison of calculated and experimental on-resonant transient absorption signals for the $J = 0 \to J = 1$ rotational transition in pure OCS. The observed and calculated absorption coefficients (from eq 4) are plotted here with $P_i(t)$ from eq 9. According to $P_i(t)$ in eq 9, the observed response contains a combination of T_1 and T_2 processes, and both relaxation times were extracted from the data (see McGurk et al.[10]).

rentzian is obtained, $\Delta\nu_{1/2} = (1/2\pi)(1/T_2)$.

In the case of the observation of microwave rotational transient signals, it is many times most convenient to apply Stark switching to bring the two-level system into, out of, or through the fixed microwave frequency. Of course, oscillator frequency modulation or diode power switching may also be used. Transient signals are observed at a diode detector, and the signal is amplified in a wide band amplifier and then digitized in a transient recorder. The digital signal is then stored in the magnetic storage of a small computer for signal averaging with subsequent repetitions of the Stark switching for either transient absorption or transient emission.

The signal at the diode detector is proportional to the square of the total electric field incident on the detector, averaged over all times faster than the response of the crystal, giving[27]

$$S = 2\beta \left[\epsilon^2 + 2\left(\frac{2\pi\omega l}{c}\right)\epsilon P_i \right.$$
$$\left. + \left(\frac{2\pi\omega l}{c}\right)^2 (P_i{}^2 + P_r{}^2) \right] \quad (7)$$

where β is the efficiency or conversion gain of the detector and all high frequencies have been averaged by

the response characteristics of the diode. The first term is a dc or constant term representing the response of the detector to the incident microwave power. The last term is normally much smaller than the second term, so it is usual to ignore it and write the time-dependent response of the detector, which is what we are interested in, as

$$\Delta S(t) = 4\beta\left(\frac{2\pi\omega l}{c}\right)\epsilon P_i \quad (8)$$

Thus, we see that the change in signal at the detector is directly proportional to the imaginary component of polarization, P_i.

Transient Absorption

The most common form of the transient absorption experiments is the on-resonant case where a two-level system is brought into resonance in a time short relative to the relaxation processes. When $\Delta\omega = 0$, eq 3 can be solved exactly subject to the appropriate initial conditions. Usually, the initial conditions (before the on-resonant absorption) are obtained from the far off-resonance limit of the steady-state results where $(\Delta\omega)^2 \gg (1/T_2)^2$ and $(\Delta\omega)^2 \gg (T_1/T_2)\varkappa^2\epsilon^2$. Under these initial conditions we have $P_r(t_i = 0) = P_i(t_i = 0) = 0$ and $\Delta N(t_i = 0) = \Delta N_0$. If, in addition, the power is sufficiently high that $\varkappa^2\epsilon^2 \gg \frac{1}{4}((1/T_2) - (1/T_1))^2$, the solutions to eq 3 are given by eq 9. Ω is defined in eq 6.

$$0 \le t; \Delta\omega = 0, P_r(0) = P_i(0) = 0, \Delta N(0) = \Delta N_0$$

$$P_r(t) = 0$$

$$P_i(t) = \frac{\hbar\varkappa^2\epsilon\Delta N_0}{4} \left[\frac{e^{-t/T}[(1/T_2)(\cos(\varkappa\epsilon t)) - ((T_1/T_2)\varkappa\epsilon + (1/T_2)(\phi/\varkappa\epsilon))(\sin(\varkappa\epsilon t))] - 1/T_2}{\Omega_p{}^2}\right]$$

$$\Delta N(t) = \Delta N_0 \left[\frac{(T_1/T_2)\varkappa^2\epsilon^2 e^{-t/T}[\cos(\varkappa\epsilon t) + (1/\varkappa\epsilon T)(\sin(\varkappa\epsilon t))] + (1/T_2)^2}{\Omega_p{}^2}\right] \quad (9)$$

$$\frac{1}{T} = \frac{1}{2}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

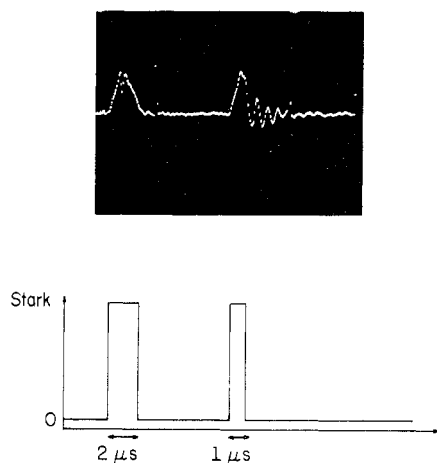$$\phi = \frac{1}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Figure 2. Experimental demonstration of responses following resonant polarization of the OCS $J = 0 \rightarrow J = 1$ transition by π and $\pi/2$ pulses after 2 μs and 1 μs, respectively. The 2-μs π pulse excitation corresponds to terminating the on-resonance stimulation, shown in Figure 1, for instance, at the first $P_i(t) = 0$ point. No further signal is seen after the 2-μs π pulse. However, if the stimulation is terminated at the first maximum in $P_i(t)$, shown again in Figure 1, the nonzero polarization leads to spontaneous coherent emission observed after the 1-s $\pi/2$ pulse. The data are from McGurk et al.[10]

If, furthermore, very high power radiation is used such that $\varkappa \epsilon T_1 \gg 1$ and $\varkappa \epsilon T_2 \gg 1$, and the interaction is terminated in a time short relative to the relaxation time, $t \ll T$, eq 9 reduce to the normal equations that are used to describe π and $\pi/2$ pulses:

$$P_r(t) = 0$$

$$P_i(t) = -\frac{\hbar \varkappa \Delta N_0}{4}(\sin(\varkappa \epsilon t))$$

$$\Delta N(t) = \Delta N_0 (\cos(\varkappa \epsilon t)) \qquad (10)$$

The $\pi/2$ pulse, where $\varkappa \epsilon t = \pi/2$, leads to maximum imaginary polarization, P_i, and zero population difference between the two levels.

$$P_r(t_{\pi/2}) = 0$$

$$P_i(t_{\pi/2}) = -\frac{\hbar \varkappa \Delta N_0}{4}$$

$$\Delta N(t_{\pi/2}) = 0 \qquad (11)$$

At a later time, we have the π pulse condition, where $\varkappa \epsilon t = \pi$, which leads to zero polarization and a population inversion,

$$P_r(t_\pi) = 0$$

$$P_i(t_\pi) = 0$$

$$\Delta N(t_\pi) = -\Delta N_0 \qquad (12)$$

Experimental on-resonant transient absorption signals with off-resonance steady-state initial conditions are shown in Figure 1. The results in Figure 1 were fit with eq 9 and 4 in order to obtain values of T_1 and T_2 for the $J = 0 \rightarrow J = 1$ rotational transition in the OCS molecule.[10] Transient nutation in NMR was first studied by Torrey,[28] who demonstrated the "wiggles" in the approach to equilibrium and the variation of the signal as one moves off-resonance. The solutions obtained in this section are formally identical with those

of Torrey, and the experimental effects are in all cases exactly analogous.

Transient Emission

In our previous discussion we have examined the signal at the detector when the initial conditions were far off-resonance where no initial polarization or change in equilibrium population is obtained ($P_r(0) = P_i(0) = 0$ and $\Delta N(0) = \Delta N_0$). In all cases we find a net decrease of signal at the detector or a net absorption of radiation energy, and we referred to the phenomena as transient absorption. In this section we will examine initial conditions in which the system is polarized and the population difference is driven to a nonequilibrium condition. Under these conditions, there is spontaneous coherent emission of radiation by the system. We call this phenomenon transient emission. We also have the possibility of creating the initial conditions with a different oscillator with different power and frequency than is used for the subsequent transient experiments.

We will consider here only the far off-resonant observation following the on-resonant initial condition. The intermediate case which includes the effects of both transient emission and off-resonant transient absorption is treated elsewhere.[27] We can easily solve eq 3 when $\Delta \omega \gg 1/T_1, 1/T_2$, and $\Delta \omega \gg \varkappa \epsilon$ to give

$$P_i(t) = e^{-t/T_2}(P_i(0) \cos(\Delta \omega t) + P_r(0) \sin(\Delta \omega t)) \qquad (13)$$

where $P_i(0)$ and $P_r(0)$ are the initial conditions. Equations 11 for an on-resonant $\pi/2$ pulse provide the initial conditions leading to the largest possible emission signal. On the other hand, eq 12 show that there will be no emission following a π pulse. Figure 2 shows experimentally the emission signal observed following a $\pi/2$ or π pulse. The NMR analogs of these experiments have been considered by Bloch[21] and Hahn.[29]

The transient emission signal may be used to measure T_2 directly. However, the entire steady-state spectrum may also be recovered from this emission signal by Fourier transforming. Substituting eq 11 into eq 13 and this result into eq 8 gives

$$\Delta S(t) = -\left(\frac{\hbar \varkappa \Delta N_0}{4}\right)\left(\frac{8\pi\beta l}{c}\right) \cos(\Delta \omega t) \, e^{-t/T_2} \qquad (14)$$

Assuming $\Delta S(t) = 0$ for $t < 0$, the frequency spectrum of ΔS is given by the cosine Fourier transform of $\Delta S(t)$. Fourier-transforming eq 14, assuming $\Delta \omega$ is positive, and neglecting the smaller term gives

$$\Delta S(\bar{\omega}) = -\left(\frac{\hbar \varkappa \Delta N_0}{4}\right)\left(\frac{4\pi\beta \omega l}{c}\right)$$
$$\times \left[\frac{1/T_2}{(1/T_2)^2 + (\Delta \omega - \bar{\omega})^2}\right] \qquad (15)$$

Equation 15 is the usual steady-state Lorentzian lineshape function in the low power limit centered at $\Delta \omega$.

When more than one transition is initially polarized, the emission from all the transitions may be detected simultaneously and Fourier transformed. The resulting spectrum will be the sum of the individual lines, each centered at its own $\Delta \omega$ relative to the common microwave frequency. This result has important ramifications

(27) T. G. Schmalz and W. H. Flygare, "Laser and Coherent Spectroscopy", J. I. Steinfeld, Ed., Plenum Press, New York, N.Y., 1976.
(28) H. C. Torrey. *Phys. Rev.* 76, 1059 (1949).
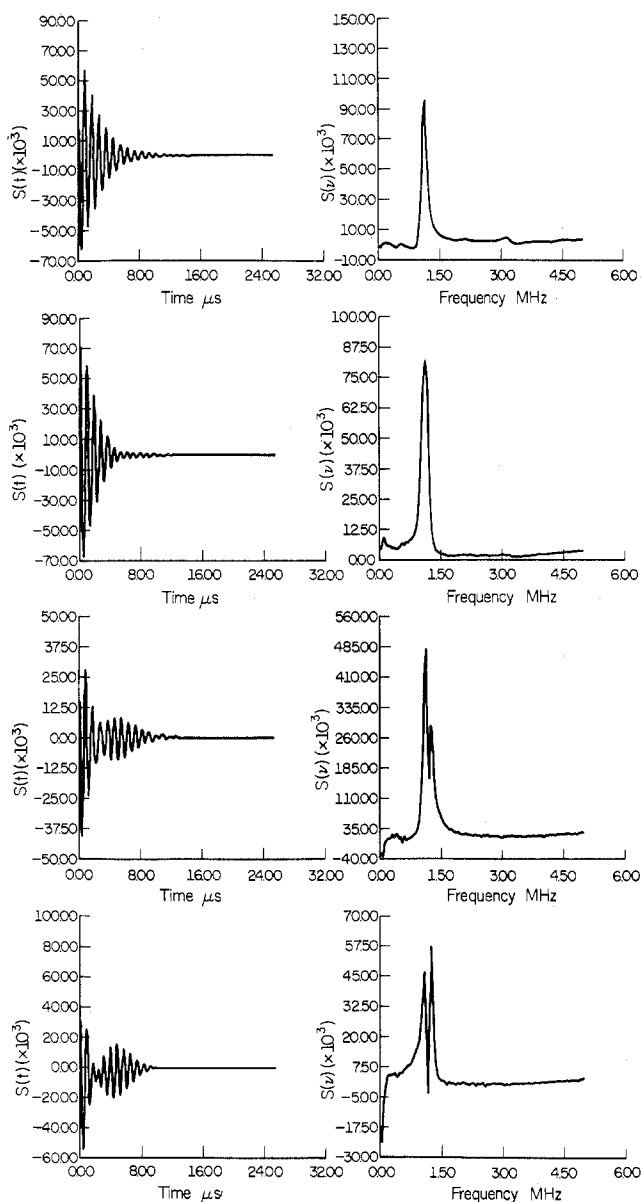(29) E. L. Hahn. *Phys. Rev.* 77, 297 (1950).

Figure 3. Emission following $\pi/2$ pulses and resultant Fourier transforms for the (J,K) = (3,3), (2,1), (3,1), and (4,1) inversion transitions (top to bottom) in $^{15}NH_3$. Doublet spectra and the corresponding beats in the signal at the detector are observed in the (3,1) and (4,1) transitions. The emission signals are given in eq 14 and the corresponding Fourier transforms are in eq 15. The data are from McGurk et al.[14]
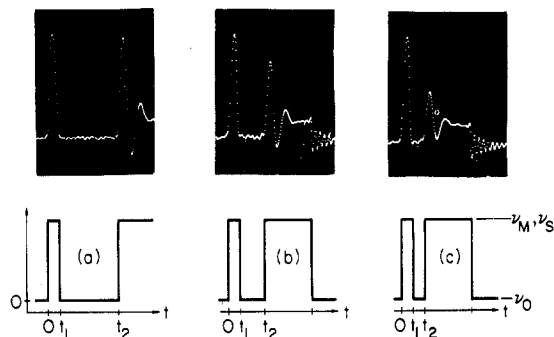

Figure 4. Diagram and oscilloscope photographs showing the pulse sequence signals as obtained from Stark switching the $J = 0 \rightarrow J = 1$ transition in OCS at 5.5-mTorr pressure. The delay times, $\tau = t_2 - t_1$, between the pulses are (a) 13.0 μs, (b) 5.5 μs, (c) 2.5 μs. The length of the first pulse is t_1 = 2.5 μs and the length of the second pulse is 10 μs. ν_m denotes the microwave frequency, ν_s the Stark-shifted frequency, and ν_0 the zero-field frequency of the $M = 0$, $J = 0 \rightarrow 1$ transition of OCS. In (b) and (c) the transient emission which occurs after the second pulse is switched off is also observed. The data are from Mäder et al.[16]

for Fourier-transform microwave spectroscopy.[14] If several lines in a given frequency band can be simultaneously polarized, it is well known that the spectrum can be recorded using Fourier-transform techniques with a gain in a signal-to-noise equal to the square root of the ratio of the line widths to the bandwidth of the polarization.[30] This principle forms the basis of Fourier-transform NMR spectrometers which are in widespread use. An example of the application of this technique in microwave spectroscopy is presented in Figure 3, which shows the emission spectrum and Fourier transform for several $^{15}NH_3$ inversion transitions. The Fourier transforms faithfully reproduce the spectrum even when the line is a doublet due to hyperfine splitting. Notice the interference pattern in $\Delta S(t)$ when there is more than one transition in the spectrum. More details on Fourier transform microwave spectroscopy using

pulsed microwave and fast analog-to-digital conversion and averaging techniques can be found elsewhere.[27,31]

Although a transient emission experiment itself provides a measure only of T_2, a variant of the experiment can be used to extract T_1. Consider a system to which a π pulse is applied at $t = 0$. Equation 12 shows that no emission will follow the pulse but that the population will be completely inverted. After the pulse, if the molecules are shifted far out of resonance, P_r and P_i will remain zero. ΔN will decay with the relaxation time T_1. After an interval τ, a $\pi/2$ pulse is applied to the system which results in a polarization according to eq 11, but with the initial conditions $P_i = P_r = 0$, $\Delta N = \Delta N_0(1 - 2e^{-\tau/T_1})$. After the end of the $\pi/2$ pulse, the molecules are again shifted far out of resonance and they undergo coherent spontaneous emission with the decaying imaginary polarization given by

$$P_i(t) = - \frac{\hbar \varkappa \Delta N_0}{4}$$

$$\times (1 - 2e^{-\tau/T_1})e^{-(t-t_{\pi/2})/T_2} \cos(\Delta\omega(t - t_{\pi/2})) \quad (16)$$

A measure of the amplitude of the transient emission signal as a function of the delay time τ between the π pulse and the $\pi/2$ pulse will thus permit the extraction of T_1. This experiment is the exact analog of the π, τ, $\pi/2$ pulse train experiment in NMR. Figure 4 shows the experimentally observed height of the second pulse as a function of delay time for the $J = 0 \rightarrow J = 1$ transition in OCS. Of course, the first pulse in these experiments is not a true π pulse due to complicating factors such as the field distribution in the waveguide, finite rise and fall times for the Stark pulse, and relaxation processes that are not completely negligible during the pulse. All of these factors have been investigated and have been found not to affect the measurement of T_1 as long as the first pulse ends when P_i is zero.[16] In the experiments shown in Figure 4 the length of the first pulse was determined empirically by adjusting until no emission was observed.

The above pulse method appears to be a faster and more accurate method of obtaining T_1 than transient nutation. T_1 is still much harder to measure than T_2

(30) R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

(31) J. Ekkers and W. H. Flygare, *Rev. Sci. Instrum.*, 47, 448 (1976).

because many pulse delays must be used at each pressure to map out the pressure-dependent part of T_1. Nevertheless, the combination of free induction decays and delayed pulses appears to be capable of providing reliable measures of T_1 and T_2 for many molecular systems. Doppler effects do sometimes provide complications at higher frequencies, but T_1 and T_2 can still be readily extracted by using multiple pulse techniques. We have not described all possible experiments for extracting T_1 and T_2 from transient experiments. For instance, fast passage methods are also capable of extracting relaxation times.[11,13,24] The above description should, however, convince the reader that the capability now exists of measuring T_1 and T_2 in rotational transitions by transient methods. We have also attempted to illustrate the analogies between transient experiments in microwave spectroscopy and nuclear magnetic resonance.

Results and Molecular Interpretation of T_1 and T_2

Since both T_1 and T_2 are introduced into the theory used here phenomenologically, there is no assurance that either will have a simple interpretation on the molecular level. Yet it is the possibility of such an interpretation as a means of obtaining molecular information that is the primary motivating factor for the measurement of T_1 and T_2. Although a large body of work is in the literature concerning the theoretical interpretation of low-power line widths,[32] comparatively little effort has been extended toward understanding T_1 on the molecular level.[33]

Work done is this group, plus that of other groups, seems to indicate that $T_1 = T_2$ for the low J states of pure OCS.[10,16] Brewer and Shoemaker[23] find $T_1 = T_2$ for a rotation–vibration transition in methyl fluoride. There is also evidence that T_1 and T_2 are equal for rotational transitions in OCS in an excess of He and CH_3F.[16] However, in spite of early steady-state experiments which showed that $T_1 = T_2$ for the inversion doublets in ammonia,[34] recent transient experiments show that T_1 and T_2 fall in the range $1.0 \leq T_2/T_1 \leq 2.0$ for a wide range of $(J, K, |M| = J)$ inversion doublets in $^{15}NH_3$.[17,33] We will attempt here to use simple kinetics to gain some insight into these experimental results.

The rate of change of the population difference between two levels can be expressed exactly in terms of the populations of the states accessible to the system and the transition rates between states. Let the two-level system be designated as lower state a and upper state b. Let all the other states be indicated by i. Then N_a, N_b, and N_i will represent the number densities of the states and R_{ab}, R_{ai}, etc., will represent the transition rates. T_1 is defined by $d\Delta N/dt = -(\Delta N - \Delta N_0)/T_1$, where $\Delta N = N_a - N_b$. Explicitly summing all possible transitions gives

$$\frac{d\Delta N}{dt} = -2(N_a - N_a^0)R_{ab} + 2(N_b - N_b^0)R_{ba}$$

$$- \sum_i (N_a - N_a^0)R_{ai} + \sum_i (N_b - N_b^0)R_{bi}$$

$$+ \sum_i (N_i - N_i^0)R_{ia} - \sum_i (N_i - N_i^0)R_{ib} \quad (17)$$

where the superscript zero indicates the equilibrium

population. To write eq 17 in a form which can be compared with the definition of T_1 requires some approximation.[27] It is assumed that there is little net transfer of population out of the states a and b during the course of the experiment. Then $N_a + N_b \simeq N_a^0 + N_b^0$ and $N_i \simeq N_i^0$, where $i \neq$ a, b. Substituting these conditions into eq 17 yields

$$\frac{1}{T_1} = R_{ab} + R_{ba} + \frac{1}{2} \sum_i R_{ai} + \frac{1}{2} \sum_i R_{bi} \quad (18)$$

Notice that transitions connecting states a and b contribute twice as heavily to T_1 as other transitions because these transitions increase the population of one state and decrease that of the other, changing ΔN by 2. This should be contrasted with the expression for T_2 given below.

It is more difficult to decide which collisions should be counted as contributing to T_2. It seems that any collision changing the state of a polarized molecule will contribute to T_2. In addition, it is possible that a collision could destroy the phase coherence of a molecule but still leave it in its initial energy state (though there is no clear experimental evidence that this ever occurs). On the other hand, only the first collision of this type should count since once the molecule has lost its phase memory it cannot recover it.

The quantity to be examined is the magnitude of the polarization given by $P = (P_r^2 + P_i^2)^{1/2}$. Equations 3 show that T_2 is defined by $dP/dt = -(P/T_2)$. As indicated above, the total polarization will be proportional to the total number of molecules initially polarized which have not yet suffered a collision. One has then

$$\frac{d\tilde{N}}{dt} = \frac{d}{dt}(\tilde{N}_a + \tilde{N}_b) = -\frac{\tilde{N}}{T_2} \quad (19)$$

where $\tilde{N}$, etc., represent the number densities of polarized molecules. The time dependence of $\tilde{N}$ is given by

$$\tilde{N}(t) = \tilde{N}_a(t) + \tilde{N}_b(t) = \tilde{N}(0)$$
$$- \int_0^t \gamma_a \tilde{N}_a(t')dt' - \int_0^t \gamma_b \tilde{N}_b(t')dt' \quad (20)$$

where $\gamma_a = R_{aa} + R_{ab} + \Sigma_i R_{ai}$ and $\gamma_b = R_{ba} + R_{bb} + \Sigma_i R_{bi}$. R_{aa} and R_{bb} represent the rates for "phase changing collisions" and the quantities γ_a and γ_b are thus the total collision rates for molecules in states a and b, respectively.

Taking the time derivatives of eq 20 gives

$$\frac{d\tilde{N}}{dt} = -\left(R_{aa} + R_{ab} + \sum_i R_{ai}\right)\tilde{N}_a$$
$$- \left(R_{bb} + R_{ba} + \sum_i R_{bi}\right)\tilde{N}_b \quad (21)$$

Again, some approximation is needed to put eq 21 into a form like eq 19.[27] Assuming that relaxation processes are approximately the same for both observed levels and that the population difference between the two levels is always very much smaller than the population of either level, we can rewrite eq 21 as the average of the

(32) For a review, see H. Rabitz, *Annu. Rev. Phys. Chem.*, **25**, 155 (1974).
(33) W. E. Hoke, D. R. Bauer, J. Ekkers, and W. H. Flygare, *J. Chem. Phys.*, **64**, 5276 (1976).
(34) For a summary, see C. Townes and A. Schawlow, "Microwave Spectroscopy" (1955), Dover Publications, republication, New York, N.Y., 1975,

coefficients of $\tilde{N}_a$ and $\tilde{N}_b$ times $(\tilde{N}_a + \tilde{N}_b)$. Comparing the result with eq 19 gives

$$\frac{1}{T_2} = \frac{1}{2} R_{aa} + \frac{1}{2} R_{bb} + \frac{1}{2} R_{ab}$$

$$+ \frac{1}{2} R_{ba} + \frac{1}{2} \sum_i R_{ai} + \frac{1}{2} \sum_i R_{bi} \quad (22)$$

Subtracting eq 18 for $1/T_1$ from eq 22 for $1/T_2$ gives

$$(1/T_2 - 1/T_1) = \frac{1}{2} (R_{aa} + R_{bb} - R_{ab} - R_{ba}) \quad (23)$$

Thus, the difference between T_1 and T_2 is given entirely in terms of transition probabilities involving the states in the two-level system being considered. It is not obvious from eq 23 that there is any necessary relation between T_1 and T_2. If there are very weak collisions, it is possible that R_{aa} and R_{bb} could be much larger than R_{ab} or R_{ba}. On the other hand, it is possible that weak collisions could be dominated by the longest range force. For molecules with permanent electric dipoles, this would be the dipole–dipole interaction which is governed by $\Delta J = \pm 1$ selection rules. If this were the case, R_{ab} and R_{ba} could be much larger than R_{aa} and R_{bb} and $1/T_1$ would be larger than $1/T_2$. Inversion transitions in NH_3 are also strongly dipole allowed, and this is the apparent reason for the $1 \leq T_2/T_1 \leq 2$ observation in the inversion levels in $^{15}NH_3$. However, if one introduces the assumption of "strong collisions", one finds $T_1 = T_2$. This can perhaps be seen most clearly by rearranging eq 23 to give

$$\left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{1}{2} \left[\left(\gamma_a - \sum_i R_{ai} \right) \right.$$
$$\left. + \left(\gamma_b - \sum_i R_{bi} \right) \right] - R_{ab} - R_{ba} \quad (24)$$

Strong collisions are interpreted to mean those sufficiently strong to leave the molecule in any of a large number of final states regardless of its initial state. Under these conditions, R_{aa}, R_{ab}, R_{ba}, and R_{bb} will all be much smaller than the total collisional rates, γ_a and γ_b, and $\gamma_a \cong \Sigma_i R_{ai}$, $\gamma_b \cong \Sigma_i R_{bi}$. Then the difference between T_1 and T_2 will be much smaller than either T_1 or T_2, and $T_1 \cong T_2$. This assumption would appear to be especially reasonable in the microwave region where $kT \gg \hbar\omega_0$. It seems to offer the best explanation for the observed equalities of T_1 and T_2 in OCS.

These ideas can be employed to analyze other types of rotational relaxation experiments. Kukolich and co-workers[35-37] have used a beam maser technique to examine a number of systems where T_1-type cross sections are apparently quite different from T_2-type cross sections for some polar gases. One of the largest differentials between the T_1- and T_2-type scattering processes was found in the $J = 1 \rightarrow 2$ OCS transition for the OCS–CH_3F collision pair where the T_1-type cross section was considerably larger than the T_2-type cross section. These results on the $J = 1 \rightarrow 2$ OCS transition are quite different from the result obtained by Mäder et al.[16] for the OCS–CH_3F pair where $T_1 \cong T_2$ for the

$J = 0 \rightarrow J = 1$ OCS transition. Assuming that the relative T_1 and T_2 processes are the same in the OCS–CH_3F system for both the $J = 0 \rightarrow J = 1$ and $J = 1 \rightarrow J = 2$ OCS transitions, we must conclude that the difference between the microwave result and the beam maser results lies in the difference between the two experiments. In the beam maser experiments, only forward scattered (at small angles) molecules were analyzed for the T_1- and T_2-type scattering cross sections. These low-angle products would result from grazing collisions which would in turn be expected to be dominated by long-range forces.[16,38] These long-range forces would be dipole–dipole forces in highly polar molecules, and it is precisely this kind of force which could lead to $1/T_1 > 1/T_2$. Comparing the microwave results indicates that the forward scattering processes have larger T_1-type cross sections than T_2-type cross sections, but the average isotropic T_1- and T_2-type scattering cross sections are nearly identical.[16] Thus, larger angle scattering cross sections would probably lead to larger T_2-type scattering cross sections. In summary, we would expect forward-scattered particles to experience stronger T_1 processes and back-scattered particles to favor stronger T_2 processes in polar gases. These conclusions could be checked by doing an angular dependent study in the beam maser experiment.

The interested reader is referred to recent work by Liu and Marcus[38] where the validity of a Bloch equation type treatment of molecular relaxation is examined. They derive a general discription of molecular relaxation under the impact approximation. With the additional assumption that the relaxation behavior of the two levels in the observed transition is not much different, they are able to obtain expressions for T_1 and T_2 in terms of molecular relaxation matrix elements. The theoretical understanding of T_1 and T_2 which now seems to be developing offers the potential in the next few years for a fruitful collaboration between theory and experiment in the investigation of gas-phase molecular relaxation processes.

Conclusion

In this Account we have summarized the main concepts in microwave rotational transient experiments which lead to a measurement of the phenomenological relaxation times T_1 and T_2 which enter the electric dipole analogs of the Bloch equations. When electromagnetic radiation interacts with a molecule through a two-level electric dipole interaction, two things happen to an ensemble of these molecules. First, a macroscopic polarization is produced which has a relaxation time T_2. Second, a nonthermal equilibrium population distribution is produced which decays back to equilibrium with a relaxation time T_1. All observations of transient phenomena involve the interplay of the polarization and population differences through their coupling in the electric dipole Bloch equations.

We center our discussion of microwave–molecule resonant transient phenomena around two main processes: *transient absorption*, which is normally called transient nutation in magnetic resonance experiments, and *transient emission*, which is normally called the

(35) S. G. Kukolich, J. H. S. Wang, and D. E. Oates, *Chem. Phys. Lett.*, **20**, 519 (1973).

(36) A. Ben-Reuven and S. G. Kukolich, *Chem. Phys. Lett.*, **23**, 376 (1973).

(37) J. H. S. Wang, D. E. Oates, A. Ben-Reuven, and S. G. Kukolich, *J. Chem. Phys.*, **39**, 5268 (1973).

(38) W. K. Liu and R. A. Marcus, *J. Chem. Phys.*, **63**, 272 (1975); **63**, 290 (1975).

free-induction decay in magnetic resonance experiments.

Transient absorption occurs when a two-level system is driven from a condition of equilibrium population difference and negligible polarization to a new state (in a time short relative to the relaxation processes) which contains a macroscopic polarization and a nonequilibrium population difference. During this process, energy is being taken from the radiation to produce a higher energy system. Thus, we refer to this process which has involved a net absorption of energy as transient absorption. The rates and behavior of the system as it moves toward its new state of macroscopic polarization and nonthermal equilibrium are determined by solving the coupled differential equations leading to the extraction (by comparison with experiment) of T_1 and T_2.

Transient emission occurs when the system is taken from a condition of interaction with the radiation where the system is polarized and in nonthermal equilibrium, to a condition where the external radiation is either removed or at least taken far off-resonance and out of interaction with the molecular two-level system. Some of the energy stored in the molecules is released by spontaneous coherent emission. In the process described above, the signal at the detector after the radiation-molecule interaction is terminated arises from a beat between the radiation field coherently emitted from the system with the radiation field of the reference microwave oscillator. The signal obtained can be Fourier transformed to give the spectrum of the original transitions which were polarized. This demonstration of microwave Fourier transform spectroscopy can lead to the same advantages as experienced in nuclear magnetic resonance.

In the last section, we have attempted a microscopic interpretation of T_1 and T_2 in terms of the transition rates between states. In the limit of strong collisions, where relaxation from one state to a large number of states is possible, we find $T_1 = T_2$, which is the most reasonable explanation for the observation that $T_1 = T_2$ in a number of molecular systems. On the other hand, if specific selection rules favor transfer from one to the other state involved in the two-level interaction, T_1 may be shorter than T_2. In order for T_1 to be longer than T_2, the molecules would have to experience collisions which relax the polarization without relaxing the populations. We are hopeful that continued theoretical and experimental study will lead to an improved understanding of molecular relaxation processes.

Structure of Solid Surfaces

Larry L. Kesmodel and Gabor A. Somorjai*

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

The past decade has witnessed exciting developments in the field of surface science. Much of this advance has been due to new techniques of electron and atom scattering that provide fundamental information on the structural and electronic properties of solid surfaces. In addition, high-speed digital computers have allowed for increasingly realistic calculations to test theoretical models of the surface properties. Surface studies are particularly motivated by the need for a better understanding of the phenomena involved in such important and diverse applications as heterogeneous catalysis, photography, and solid-state devices of high surface-to-volume ratio, to mention only a few. In this Account we shall focus on the characterization of the structure of solid surfaces (or surface crystallography) by the technique of low-energy electron diffraction (LEED), which has been found to be the most powerful method of investigating surface geometry of crystalline solids on an atomic scale.[1-4] Other important surface spectroscopies often utilized in conjunction with LEED include Auger electron spectroscopy (AES) for the characterization of surface chemical composition[5] and ultraviolet photoelectron spectroscopy (UPS) for studies of surface electronic structure.[6]

The structure of solid surfaces is pertinent to virtually all descriptions of surface phenomena and gives LEED a status in surface science analogous to that of x-ray diffraction in the description of bulk atomic structure.

Gabor A. Somorjai is Professor of Chemistry at University of California, Berkeley, and Principal Investigator in the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory. He was born in Budapest, and studied at the University of Technical Sciences there for his B.S. degree. After moving to the United States, he earned the Ph.D. at Berkeley in 1960, and then joined the research staff at IBM, Yorktown Heights, N.Y. He returned to Berkeley in 1964. His principal research interests are in the field of surface science.

Larry L. Kesmodel received his B.S. degree from California Institute of Technology in 1969 and the Ph.D. from University of Texas in 1973. He was a postdoctoral fellow at University of California, Berkeley, from 1973 to 1975, and is now a staff member of the Materials and Molecular Research Division.

(1) G. A. Somorjai and L. L. Kesmodel, *MTP Int. Rev. Sci., Phys. Chem., Ser. Two*, 7 (1975).

(2) M. A. Chesters and G. A. Somorjai, *Annu. Rev. Mater. Sci.*, 5, 99 (1975).

(3) J. A. Strozier, Jr., D. W. Jepsen, and F. Jona, in "Surface Physics of Materials", Vol. I, J. M. Blakely, Ed., Academic Press, New York, N.Y., 1975.

(4) J. B. Pendry, "Low-Energy Electron Diffraction Theory", Academic Press, London, 1974.

(5) See, for example, C. C. Chang, *Surf. Sci.*, 25, 53 (1971).

(6) See, for example, D. E. Eastman in "Electron Spectroscopy", D. A. Shirley, Ed., North Holland Publishing Co., New York, N.Y., 1972.