PHYSICAL REVIEW A VOLUME 15, NUMBER 4 APRIL 1977

Semiclassical theory of two-photon absorption: Absorption and level shifts in a model system

M. D. Burrows* and W. R. Salzman
Department of Chemistry, University of Arizona, Tucson, Arizona 85721
(Received 1 December 1975; revised manuscript received 9 August 1976)

Numerical calculations of level shifts and power-broadening linewidths for double-photon absorption in truncated rigid-rotor models are presented. This work demonstrates the feasibility of a previously suggested calculational method. It is shown that level shifts in double-photon absorption deduced from three-state models are misleading since other states dipole-coupled to states directly involved in the transition make important contributions to the shifts.

Recent high-resolution double-photon experiments[1-4] have rekindled interest in the theory of multiple-photon processes.[5,6] The effective elimination of Doppler broadening in double-photon resonance lines[1-3] has made high-resolution double-photon spectroscopy an important research tool, the ultimate limitation in linewidth measurements in such experiments being the frequency stability of the excitation source, usually a tunable laser. The lasers used in double-photon spectroscopy are often sufficiently high powered or frequency stable that it is useful to consider the magnitude of the energy-level shifts of the type first predicted by Bloch and Siegert for single-photon processes. Because of the inherently narrower absorption resonance lines of double-photon processes, these level shifts can be quite important in determining the exact resonant frequency of the double-photon absorption. In the microwave frequency region these level shifts can be as much as one part in 10^5 of the resonance frequency, and frequency shifts on the order of a GHz have recently been observed in the optical region by Liao and Bjorkholm.[4]

Published theoretical work on double-photon absorption is almost uniformly limited to the treatment of three-level model systems, which are the simplest models giving significant double-photon transition probabilities. Based on the analogy of the utility of two-level systems in the study of single-photon absorption, it seems very reasonable to use the simplest possible models for double-photon absorption. However, it is the purpose of the present work to show that, in contrast to the Bloch-Siegert level shift in single-photon processes, which is orders of magnitude smaller than the power-broadening linewidth, the level shift in double-photon processes is of the same order of magnitude as the power-broadening width and in addition depends strongly on the number of active levels included in the calculation. The dependence of level shifts on additional levels is sufficiently strong in some cases to give a level shift of opposite sign from that predicted from the three-state model.

The calculations presented here are the first to be performed using an approximation scheme proposed by one of us (W.R.S.)[7] which involves writing an approximation to the time-evolution operator for the model system under the influence of an externally supplied classical electromagnetic driving field. The essence of this technique, which can be applied to any system interacting with a classical periodic radiation field (period τ), is that once the time-evolution operator $U(\tau, 0)$ has been generated by numerical integration of the interaction representation Schrödinger equation, $U(n\tau, 0)$ can then be obtained for all later times $n\tau$ by matrix multiplication, provided n is an integer. This technique is most useful whenever the phenomena of interest occur on a time scale much larger than τ, as is the case for two-photon absorption at physically realizable electric field strengths. Although these calculations are numerical, they can be easily performed to almost any desired degree of accuracy, regardless of radiation field intensity.

The present technique is preferable to the usual perturbation theory methods[6] in the sense of including the effect of the field to all orders in the model system. However, the technique is limited by requiring truncation of real quantum mechanical systems with infinite numbers of states to finite-state model systems (even though a large number of states may be included). As mentioned above, it will be demonstrated that states other than the intermediate level which are dipole coupled to either of the states involved in the two-photon absorption have a significant effect on the net double-photon frequency shift. For this reason the modified form of the double-photon analog of the Rabi formula derived by Oka and Shimizu,[8] although accurate for a model three-level system, does not give the correct level shift for atomic and molecular systems having adjacent energy levels, other than the intermediate level, dipole-coupled to the

initial or final states of the double-photon absorption process. The level-shift relation of Oka and Shimizu can, as we will show, be modified to yield good estimates of the net frequency shifts resulting from the adjacent levels.

The calculations presented are for absorption of two equal-energy photons; however the method is applicable to absorption of two unequal-energy photons when $\omega_1/\omega_2 = n_1/n_2$ and n_1 and n_2 are positive integers. In fact, the method can be applied to any field with form such that $E(t+\tau) = E(t)$.

TIME-EVOLUTION OPERATOR THEORY

We consider the problem of an atomic or molecular system in a monochromatic radiation field $\vec{E}(t) = \vec{E}_0 \cos(\omega t)$, where for convenience $\vec{E}_0$ is along the laboratory z axis. The total Hamiltonian is $H_0 + V$, where H_0 is the Hamiltonian of the atomic or molecular system and V is the interaction between this system and the radiation field. We use the dipole approximation and set $V = -\mu_z E_0 \cos(\omega t)$. H_0, V, and μ_z are all finite Hermitian matrices (H_0 is diagonal and μ_z is real and symmetric in the models used here), and the selection of the matrix elements of H_0 and μ_z defines the model system. We are concerned with the time-evolution operator of the system $U(t_2, t_1)$, and use the shorter notation $U(t) = U(t, 0)$. The periodic interaction enables us to use the relation $U(n\tau) = U^n(\tau)$ for the time evolution operator in the Schrödinger representation, where $\tau = 2\pi/\omega$ is the period of the driving field.[7] To generate $U(\tau)$, we transform into the interaction representation and use standard finite-difference techniques to numerically integrate the time-dependent Schrödinger equation for $U_I(t)$ from $t = 0$ to $t = \tau$. Integration of

$$\frac{\delta}{\delta t} U_I(t) = \frac{1}{i\hbar} V_I(t) U_I(t) \tag{1}$$

[where $V_I(t)$ is the operator $V(t)$ transformed into the interaction representation] from time 0 to time τ gives $U_I(\tau)$. The $U(\tau)$ in the Schrödinger representation is then regenerated by matrix multiplication with the diagonal matrix $e^{-i\tau H_0/\hbar}$

$$U(\tau) = e^{-i\tau H_0/\hbar} U_I(\tau) . \tag{2}$$

$U(n\tau)$ may then be computed for all integer n by matrix multiplication. Since the time scale of double-photon transitions is much larger than τ, a convenient time interval, usually $2^m\tau$ is chosen for the problem and the appropriate transition probability

$$P_{fi}(n2^m\tau) = |\langle f | U(2^m\tau)^n | i \rangle|^2$$

is calculated at intervals of $2^m\tau$.[9] The resonant double-photon absorption frequency can be found by repeating the calculation at several frequencies and fitting $P_{max}(\omega)$ to a Lorentzian curve. It is found that $P_{max}(\omega)$ is Lorentzian to very high accuracy except when one of the active levels not directly involved in the transition is in single-photon absorption resonance with the driving field.

RESULTS FOR A TRUNCATED RIGID-ROTOR MODEL SYSTEM

The model system for the present discussion is a truncation of the $M = 0$ manifold of a rigid rotor to a model with from 3 to 6 states. The initial calculations were carried out on a model appropriate for the $K = M = 0$ manifold of the symmetric-top molecule CD_3CN (dipole moment, 3.93 D and rotational constant $B = 7857.93$ MHz) at an applied field with maximum amplitude 200 V/cm (~53 W/cm^2). However, it was readily apparent that the shifts and widths scaled proportional to $(\mu E_0)^2$ and inversely proportional to B and the majority of calculations were performed in units of $(\mu E_0)^2/\hbar^2 B$. Thus the calculations can be scaled to any frequency region or interaction strength as long as the field is not so strong that the transition time is comparable to the period τ.

The numerical integration was, in most cases, carried out by dividing the interval $0 \rightarrow \tau$ into a grid of 1000 equal parts. 100-step numerical integrations gave results different than the 1000-step grid calculations, and 10000-step grids gave no significant changes from those at 1000 steps.

The two-photon absorption transition probability in models with only three states (Fig. 1, these are models containing only the states $J = 0, 1, 2$ or $J = 1, 2, 3$ in the present work) is well described by the double-photon analog of the Rabi formula derived by Oka and Shimizu, namely,

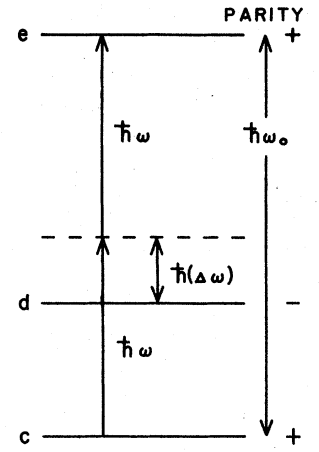

FIG. 1. Basic three-level system model for double-photon absorption; labeling and notation of Ref. 8.

$$P_{c\to e}(t) = \frac{\gamma^2}{\gamma^2 + (\frac{1}{2}\omega_0 + \delta' - \omega)^2} \times \sin^2\{t[(\tfrac{1}{2}\omega_0 + \delta' - \omega)^2 + \gamma^2]^{1/2}\} \quad (3)$$

with width γ given by

$$\gamma = \frac{(\mu_z E_0)_{cd}(\mu_z E_0)_{de}}{4\hbar^2 \Delta\omega} , \quad (4)$$

and provided the "level shift" δ' is corrected to read

$$\delta' = -\delta'_c + \delta'_e$$

with

$$\delta'_c = \frac{|(\mu_z E_0)_{cd}|^2}{4\hbar^2 \Delta\omega} \frac{\omega - \Delta\omega}{\omega_0 - \Delta\omega},$$

$$\delta'_e = \frac{|(\mu_z E_0)_{ed}|^2}{4\hbar^2 \Delta\omega} \frac{\omega + \Delta\omega}{\omega_0 + \Delta\omega},$$

and where $\Delta\omega > 0$ is the frequency separation between the actual intermediate level d and a "resonant" intermediate level, and c and e label the lower and upper levels, respectively (see Fig. 1).

The δ', δ'_c, and δ'_e shown here are not truly level shifts because they are frequency dependent; however, Eq. (3) is a Rabi formula and may be rewritten in such a manner as to explicitly display the frequency-independent level shift (see below).

The models for which calculations are reported here are truncations of a rigid-rotor system; nevertheless, the accuracy of Eq. (3) was checked by calculations on several models with level structures not appropriate for a rigid rotor but with various values of $\Delta\omega$.

The results of two-photon absorption calculations on six different truncated versions of the rigid rotor are shown in Table I. Since the widths and shifts are proportional to $(\mu E_0)^2/\hbar^2 B$ up to field strengths many orders magnitude stronger than those presently realizable experimentally, they are presented as the unitless quantitives $\hbar^2\gamma B/(\mu E_0)^2$ and $\hbar^2\delta B/(\mu E_0)^2$. It is seen from Table I that the power-broadened linewidths are moderately insensitive to the number of states included in the model, whereas the level shifts are extremely sensitive to changes in the model and may be positive, negative, or nearly zero. The inclusion of additional states not directly dipole-coupled to the states involved in the double-photon transition gives no perceptible contribution at the level of accuracy of the calculation reported here, and such models are not included in the table. Thus the level shift to be expected for the $J = 0 \to 2$ transition is that calculated for the $J = 0, 1, 2, 3$ model and the expected shift for the $J = 1 \to 3$ transition that calculated for the $J = 0, 1, 2, 3, 4$ model. In the former case the level shift is negative and in the latter case small and positive, but in neither case are the shifts correctly predicted on the basis of a three-state model.

DISCUSSION

Although the level shifts for double-photon absorption calculated from the prescription of Oka and Shimizu are not the same as those calculated for larger models, one can use the Oka and Shimizu results to estimate level shifts in the latter case. First of all, we note from Table I that the contributions of each added state to the shift of individual levels involved in the transition appears to be additive. The Rabi formula, Eq. (3), can be rewritten, ignoring fourth and higher powers of E_0, as

$$P(t) = \frac{\gamma^2}{(\frac{1}{2}\omega_0 - \delta_c + \delta_e - \omega)^2 + \gamma^2} \times \sin^2\{t[(\tfrac{1}{2}\omega_0 - \delta_c + \delta_e - \omega)^2 + \gamma^2]^{1/2}\}, \quad (5)$$

where γ is the same as above, but now the δ_c and δ_e are frequency independent and given by

TABLE I. Level shifts and power-broadening linewidths for several truncated rigid-rotor model systems, calculated both by time-evolution operator methods and estimated from formulas derived from Ref. 8. δ_0 and γ_0 are unitless quantities given by $\delta_0 = \hbar^2\delta B/(E_0\mu)^2$, etc., where B is the rotational constant, μ is the permanent dipole moment of the molecule and E_0 is the maximum amplitude of the driving electric field.

Model, J states	Transition	Calculations from $U(\tau)$ $10^2\delta_0$	$10^2\gamma_0$	Calculations from Eqs. (4), (6), and (7) $10^2\delta_0$	$10^2\gamma_0$
0, 1, 2	0 → 2	0.49	7.48	0.48	7.45
0, 1, 2, 3	0 → 2	−0.99	7.54	−0.95	7.45
1, 2, 3	1 → 3	0.54	6.51	0.54	6.55
1, 2, 3, 4	1 → 3	−0.79	6.51	−0.76	6.55
0, 1, 2, 3	1 → 3	1.35	6.55	1.38	6.55
0, 1, 2, 3, 4	1 → 3	0.03	6.56	0.08	6.55

$$\delta_c = \frac{|(E_0\mu_z)_{cd}|^2}{8\Delta\omega} \frac{\omega_0 - 2\Delta\omega}{\omega_0 - \Delta\omega}, \quad (6)$$

$$\delta_e = \frac{|(E_0\mu_z)_{de}|^2}{8\Delta\omega} \frac{\omega_0 + 2\Delta\omega}{\omega_0 + \Delta\omega}. \quad (7)$$

The additivity of contributions to the level shift δ implies that we should be able to use formulas similar to the above to estimate contributions of additional levels. The δ_c is a contribution to the shift of level c from the intermediate level d which is *above* level c. Accordingly, we use Eq. (6) to estimate added level-shift contributions to the state in question from states above that level. With the present models this means using Eq. (6) to calculate the additional level-shift contribution of the $J=3$ state to the $J=0, 1, 2$ model and the contribution of the $J=4$ state to the $J=1, 2, 3$ model. Conversely, we use Eq. (7) to estimate the contributions of the $J=0$ state to the level shift of the $J=1$ state in the $J=1, 2, 3$ models. In each case $\Delta\omega > 0$ is the frequency difference between the actual "intermediate state" and a hypothetical resonant intermediate state half-way between the initial and final states of the two-photon absorption. The results of these calculations (and calculation of γ) are given in the last two columns of Table I. The agreement is well within the accuracy claimed for the numerical calculations based on $U(n\tau)$, and we conclude that Eqs. (6) and (7) are reasonable estimates of frequency shifts.

In the models considered here, the states added to the basic three-state model are not truly "intermediate states" in the same sense as the $J=1$ state in the $J=0, 1, 2$ model or the $J=2$ state in the $J=1, 2, 3$ model simply because the "outer" states are not dipole-coupled to the initial *and* final states of the double-photon absorption process. This condition is a consequence of the selection rules for single-photon absorption,[10] but it also makes it clear that, in contrast to level shifts, the power-broadening width γ depends on truly intermediate states coupled to both initial and final states of the double-photon transition. This suggestion will be considered in further work on models with different single-photon absorption selection rules.

ACKNOWLEDGMENT

We gratefully acknowledge the University of Arizona Computer Center for the use of their facilities in performing these calculations.

*Submitted in partial fulfillment of the requirements for the M. S. degree in Chemistry.

[1]M. D. Levenson and N. Bloembergen, Phys. Rev. Lett. 32, 645 (1974).

[2]T. W. Hänsch, K. C. Harvey, G. Meisel, and A. L. Schwalow, Opt. Commun. 11, 50 (1974).

[3]N. Bloembergen, M. D. Levenson, and M. M. Salour, Phys. Rev. Lett. 32, 867 (1974).

[4]J. E. Bjorkholm and P. F. Liao, Phys. Rev. Lett. 33, 128 (1974).

[5]R. G. Brewer and E. L. Hahn, Phys. Rev. A 11, 1641 (1974).

[6]A. M. Bonch-Bruevich and V. A. Khodovoĭ, Usp. Fiz. Nauk. 93, 71 (1967) [Sov. Phys.-Usp. 10, 637 (1968)].

[7]W. R. Salzman, Phys. Rev. A 10, 461 (1974).

[8]T. Oka and T. Shimizu, Phys. Rev. A 2, 587 (1970).

[9]Straightforward numerical integration of a typical system would have taken about 82 days of computer time on the DEC-10 system. This should be compared to the actual computer time of about 35 sec using the present techniques.

[10]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).