The Journal of Chemical Physics

Two-photon absorption line shapes in the transit-time limit

Cite as: J. Chem. Phys. **154**, 104105 (2021); https://doi.org/10.1063/5.0040868
Submitted: 16 December 2020 . Accepted: 18 February 2021 . Published Online: 08 March 2021

Kevin K. Lehmann

AIP Publishing

The Journal of Chemical Physics | ARTICLE | scitation.org/journal/jcp

Two-photon absorption line shapes in the transit-time limit

Cite as: J. Chem. Phys. **154**, 104105 (2021); doi: 10.1063/5.0040868
Submitted: 16 December 2020 • Accepted: 18 February 2021 •
Published Online: 8 March 2021

View Online Export Citation CrossMark

Kevin K. Lehmann[a)]

AFFILIATIONS

Departments of Chemistry and Physics, University of Virginia, Charlottesville, Virginia 22904-4319, USA

[a)]Author to whom correspondence should be addressed: lehmann@virginia.edu

ABSTRACT

A weak excitation transit-time resolution limited analytic line shape is derived for a Doppler broadening-free degenerate two-photon transition from a standing wave with a TEM_{00} transverse profile. This approximation is appropriate when the collisional mean free path is much larger than the transverse width of the TEM_{00} beam. It is considerably simpler than the two-photon absorption line shape previously published, Bordé, C. R. Hebd. Seances Acad. Sci., Ser. B **282**, 341–344 (1976), which was derived for more general experimental conditions. The case of a saturating field, with an intensity-dependent shift of the resonance frequency, is treated and expressed in reduced units. Numerical calculations are presented for the line shape for a range of the reduced intensity and light intensity shifts values.

I. INTRODUCTION

Recently, the author published an analysis of cavity-ring down spectroscopy detection of two-photon absorption (TPA).[1] Degenerate two-photon absorption from counter-propagating waves is first-order Doppler-free,[2–4] which allows for a resolution far higher than that of Doppler broadened spectroscopy. For excitation in the IR, near a vibrational fundamental, there are resonantly enhanced transitions from the ground vibrational state to an overtone of an IR allowed fundamental, with changes in rotational energy compensating for anharmonicity, resulting in a detuning of the intermediate state absorption of less than the absorber's rotational constant. This results in a spectrum dominated by a small fraction of the transitions with thermally excited lower states, further improving the selectivity compared to one-photon absorption spectroscopy. The published analysis was based upon the steady-state solutions of the optical Bloch equations for three levels. These predict that TPA lines will be homogeneously broadened with an angular frequency half width at half maximum (HWHM) equal to one-half of the dephasing rate of the coherence between initial and final states.[3,5] Typically, for ro-vibrational transitions in the IR, the homogeneous width arises from pressure broadening and, like for the one-photon absorption coefficient (with units m^{-1}) in the limit that pressure broadening greatly exceeds the Doppler width, the peak two-photon absorption coefficient [with units of $(m\ W)^{-1}$] of a gas will be pressure independent.[1] When the pressure of the sample is reduced to the point that the collisional mean-free-path becomes of the order of the beam radius of the laser field exciting the transition, the steady-state solutions of the optical Block equations used in the previous work[1] will no longer be appropriate and one must consider the motion of the absorbers through the laser field. At sufficiently low pressure, collisions can be neglected, and the resolution of the absorption will be limited by the finite duration of the excitation field experienced by a moving molecule. A similar limit in the cases of Lamb dip[6] and molecular beam[7] spectroscopies is known as the transit-time limit.

This paper will present an analysis of two-photon absorption in the transit-time limit when a molecule passes through a standing wave excitation field, which will be assumed to be a Gaussian TEM_{00} mode.[8] It will first consider the case in the weak field limit when saturation of the TPA can be neglected and a simple analytical result can be derived. This will be followed by numerical calculations applicable to higher power, where TPA saturation and light intensity (AC Stark) induced shifts of the absorption resonance are significant. The AC Stark shift of the transition is proportional to optical intensity and the difference in AC polarizability of the initial and final states.

Let us assume that the absorber is moving with velocity $\vec{v}$ and is excited by a TEM_{00} standing optical wave of angular frequency ω, with the z axis centered on the beam and an origin at the focal point of the wave. Let r be the distance perpendicular to the z axis.

The TEM_{00} electric field of the standing wave can be written in cylindrical coordinates as[8]

$$E(r,z,t) = E_0\,\vec{\varepsilon}\,\frac{z_0}{\sqrt{z_0^2+z^2}}\,e^{-\frac{kr^2}{2(z_0-iz)}+i(kz-\eta(z))}\cos(\omega t) + \text{c.c.}, \tag{1}$$

where $k = \omega/c$ is magnitude of the wavevector of the light, $\vec{\varepsilon}$ is the polarization vector, z_0 is the confocal length of the beam, and $\eta(z) = \tan^{-1}(z/z_0)$ is the Guoy phase shift. The beam has a Gaussian intensity vs r, falling by a factor of e^{-2} for $r = w(z)$ (the beam radius), where $w(z)^2 = w_0^2\left(1+(z/z_0)^2\right)$ and $w_0 = \sqrt{2z_0/k}$ is the beam radius in the focal plane. E_0 is the electric field amplitude at the focal point ($r = z = 0$) and is related to the one-way optical power, P, by $E_0 = \sqrt{4P/\pi\varepsilon_0 c w_0^2}$.

It is assumed that the sample is at low pressure and the optical power is sufficiently low such that we have a single pair of resonantly coupled levels, with the energy difference very close to $2\hbar\omega$. It is further assumed that there exists one or more intermediate states, n, that simultaneously have dipole allowed transitions from the initial state g and to the final state f. The notations $\omega_i = E_i/\hbar$, $\omega_{ij} = \omega_i - \omega_j$, and $\Omega_{ij} = \langle i|\vec{\mu}\cdot\vec{\varepsilon}|j\rangle E_0(w_0/w(z))e^{-r^2/w(z)^2}/2\hbar$ are used. The resonant condition implies $2\omega \approx \omega_{\mathrm{gf}}$, and we assume that the detuning of all one photon transitions $|\omega-\omega_{ij}|$ is large compared to the Rabi frequencies Ω_{ng} and Ω_{fn}. In this case, quasi-degenerate perturbation theory can be used to eliminate the off-resonance states n in the dress state Hamiltonian,[9] resulting in an effective two-state Hamiltonian with matrix elements given by[10]

$$\begin{aligned} H_{\mathrm{gg}}/\hbar &= \omega_{\mathrm{g}} + \Delta\omega_{\mathrm{g}} = \omega_{\mathrm{g}} - \sum_n |\Omega_{\mathrm{gn}}|^2\left(\frac{1}{\omega_n-\omega_{\mathrm{g}}-\omega+kv_z}\right. \\ &\quad + \frac{1}{\omega_n-\omega_{\mathrm{g}}-\omega-kv_z} + \frac{1}{\omega_n-\omega_{\mathrm{g}}+\omega+kv_z} \\ &\quad \left. + \frac{1}{\omega_n-\omega_{\mathrm{g}}+\omega-kv_z}\right), \end{aligned} \tag{2}$$

$$\begin{aligned} H_{\mathrm{ff}}/\hbar &= \omega_{\mathrm{f}} + 2\omega + \Delta\omega_{\mathrm{f}} = \omega_{\mathrm{f}} + 2\omega - \sum_n |\Omega_{\mathrm{fn}}|^2 \\ &\quad \times\left(\frac{1}{\omega_n-\omega_{\mathrm{f}}-\omega+kv_z} + \frac{1}{\omega_n-\omega_{\mathrm{f}}-\omega-kv_z}\right. \\ &\quad \left. + \frac{1}{\omega_n-\omega_{\mathrm{f}}+\omega+kv_z} + \frac{1}{\omega_n-\omega_{\mathrm{f}}+\omega-kv_z}\right), \end{aligned} \tag{3}$$

$$\begin{aligned} H_{\mathrm{gf}}/\hbar &= \Omega_{\mathrm{2p}} = \frac{1}{2}\sum_n \Omega_{\mathrm{gn}}\Omega_{\mathrm{nf}}\left(\frac{1}{\omega_n-\omega_{\mathrm{g}}-\omega+kv_z}\right. \\ &\quad + \frac{1}{\omega_n-\omega_{\mathrm{g}}-\omega-kv_z} + \frac{1}{\omega_{\mathrm{f}}-\omega_n-\omega+kv_z} \\ &\quad \left. + \frac{1}{\omega_{\mathrm{f}}-\omega_n-\omega-kv_z}\right), \end{aligned} \tag{4}$$

$$\Omega_{ij}\Omega_{jk} = \langle i|\vec{\mu}\cdot\vec{\varepsilon}|j\rangle\langle j|\vec{\mu}\cdot\vec{\varepsilon}|k\rangle\,\frac{P\,e^{-2r^2/w(z)^2}}{\pi\,\varepsilon_0\,c\,\hbar^2\,w(z)^2}. \tag{5}$$

The state f has one photon fewer in the light field from each direction; this model does not include the Doppler-broadened TPA contribution, which reaches distinguishable final states with two photons removed from either directional beam and includes a Doppler shift contribution of $\pm 2kv_z$ to H_{ff}. The equation of motion for this effective two-level system is the same as that of a one photon two-level system if we use Ω_{2p} in Eq. (4) for the Rabi frequency as well as $\Delta\omega = \omega_{\mathrm{f}} - \omega_{\mathrm{g}} - 2\omega + \Delta\omega_{\mathrm{f}} - \Delta\omega_{\mathrm{g}}$ [Eqs. (2) and (3)] for the detuning from resonance. Both Ω_{2p} and $\Delta\omega_{\mathrm{f}} - \Delta\omega_{\mathrm{g}}$ are proportional to the light intensity; $\Delta\omega_{\mathrm{f}} - \Delta\omega_{\mathrm{g}}$ is often called the light or AC Stark shift.

In the limit that the TPA is dominated by a single near-resonance state n, but with $|\omega_{\mathrm{ng}}-\omega| \gg |\omega_{\mathrm{fg}}-2\omega|$ and kv_z, we have the limits $\Delta\omega_{\mathrm{fg}} = \Delta\omega_{\mathrm{f}} - \Delta\omega_{\mathrm{g}} = -2(\Omega_{\mathrm{fn}}^2 - \Omega_{\mathrm{ng}}^2)/(\omega_{\mathrm{ng}}-\omega)$ and $\Omega_{\mathrm{2p}} = 2\Omega_{\mathrm{fn}}\Omega_{\mathrm{ng}}/(\omega_{\mathrm{ng}}-\omega)$. If we further assume the double harmonic oscillator approximation[11] that we are driving the $n \to 1 \to 2$ two-photon vibrational transition and approximate the two rotational contributions to the transition matrix elements as equal, we have $\Omega_{21} = \sqrt{2}\,\Omega_{10}$, and thus, $\Delta\omega_{\mathrm{fg}} = \Omega_{\mathrm{2p}}/\sqrt{2} = 2\,\Omega_{01}^2/(\omega_{\mathrm{ng}}-\omega)$.

Given the lack of Doppler broadening and that $z_0 \gg w(z)$, we can ignore v_z when integrating the equations of motion. Each molecule will pass through the TEM_{00} mode with an impact parameter b and the magnitude of the velocity perpendicular to z of v, with v having a 2D Maxwell–Boltzmann distribution, $P_{2D}(v) = (mv/k_{\mathrm{B}}T)\exp(-mv^2/2k_{\mathrm{B}}T)$. For such a trajectory, let $\rho_{\mathrm{ff}}^{\infty}(b,v,\Delta\omega)$ be the probability that a molecule that enters the field in state g leaves in state f; $\Delta\omega = (\omega_{\mathrm{f}}-\omega_{\mathrm{g}})/2 - \omega$ is the detuning from the two photon resonance. The rate of photon absorption per unit path length by a thermal sample with the number density in state g of N_g can be written as

$$R_{\mathrm{2p}}(\Delta\omega) = 4N_g\int_0^{\infty}\int_0^{\infty} vP_{2D}(v)\rho_{\mathrm{ff}}^{\infty}(b,v,\Delta\omega)\,db\,dv. \tag{6}$$

II. WEAK FIELD LIMIT

For a weak excitation field intensity, we use first order time dependent perturbation theory to write

$$\rho_{\mathrm{ff}}^{\infty}(b,v,\Delta\omega) = \left|\int_{-\infty}^{\infty}\Omega_{\mathrm{2p}}(t)\exp(-i(2\Delta\omega t))dt\right|^2, \tag{7}$$

$$\Omega_{\mathrm{2p}}(t) = \Omega_{\mathrm{2p}}^{(0)}\exp(-2b^2/w^2)\exp(-2v^2t^2/w^2), \tag{8}$$

$$\begin{aligned} \rho_{\mathrm{ff}}^{\infty}(b,v,\Delta\omega) &= \left(\Omega_{\mathrm{2p}}^{(0)}\right)^2\exp(-4b^2/w(z)^2) \\ &\quad \times\frac{\pi w(z)^2}{2v^2}\exp\left(-\frac{w(z)^2\Delta\omega^2}{4v^2}\right), \end{aligned} \tag{9}$$

$$\int_{-\infty}^{\infty}\rho_{\mathrm{ff}}^{\infty}(b,v,\Delta\omega)db = \left(\Omega_{\mathrm{2p}}^{(0)}\right)^2\frac{(\pi w(z)^2)^{3/2}}{4v^2}\exp\left(-\frac{w(z)^2\Delta\omega^2}{4v^2}\right). \tag{10}$$

Recalling that $\Delta\omega$ is linear in ω, we see that for a molecule crossing with perpendicular speed v, the transit-time limited nonsaturated line shape is Gaussian in detuning with an angular frequency HWHM of $2\sqrt{\ln(2)}v/w(z)$. For single-photon absorption in the transit time limit, the line shape is also Gaussian in detuning with a HWHM of $\sqrt{2\ln(2)}v/w_0$, independent of the beam crossing position z. The latter is due to the fact that as one moves away from the focus and the beam radius increases, the laser beam develops a wavefront curvature that leads to an effective frequency sweep experienced by the molecules crossing it and this just compensates for the expected reduction in linewidth due to the longer interaction time. In the two-photon case, the frequency shifts due to motion through the forward and backward propagating fields cancel and thus do not increase the two-photon linewidth. The two-photon line shape is independent of the collimation of the molecular beam, while realizing the transit-time limit for one-photon transitions requires that the angular spread of the molecular beam be $<\lambda/2\pi w_0$, which implies that the angular spread of the molecular beam be less than the far-field diffraction spread angle of the TEM_{00} beam. As $\left(\Omega_{2p}^{(0)}\right)^2$ is proportional to $w(z)^{-4}$, we see that the on-resonance excitation probability $\rho_{ff}^{\infty}(b, v, 0)$ scales $w(z)^{-2}$ and v^{-2}. This can be contrasted with transit-time limited one-photon absorption where the on-resonance absorption probability is independent of $w(z)$ and also scales as v^{-2}.

Integration over the 2D speed distribution gives the thermally averaged excitation rate [Eq. (6)],

$$R_{2p}(\Delta\omega) = \frac{\pi^3 N_g w(z)^3 \left(\Omega_{2p}^{(0)}\right)^2}{2}\sqrt{\frac{m}{2k_b T}} \times \exp\left(-\sqrt{\frac{m}{2k_b T}}w(z)|\Delta\omega|\right), \quad (11)$$

$$\Delta\omega_{\mathrm{HWHM}} = \frac{\ln(2)}{2w(z)}\sqrt{\frac{2k_b T}{m}}, \quad (12)$$

where $\Omega_{2p}^{(0)}$ is the two-photon Rabi rate when the molecule is at the center of the laser beam. $\Delta\omega_{\mathrm{HWHM}}$ is the angular frequency HWHM (of ω) of this line shape. The line shape is predicted to have a cusp, i.e., a discontinuous slope, at exact resonance $\Delta\omega = 0$. This arises from the $1/v^2$ factor in $\rho_{ff}^{\infty}(b, v, \Delta\omega)$, which cancels the factor of v^2 in $vP(v)$, combined with the transit-time width approaching zero width as $v \to 0$. Clearly, both the assumptions that collisions can be neglected and that $\rho_{ff}^{\infty}(b, v, \Delta\omega)$ can be calculated by perturbation theory break down in this limit of small v. Correcting these assumptions will "round-off" the cusp. It is noted that $\Omega_{2p}^{(0)}$ is proportional to the on-axis intensity and thus inversely proportional to $w(z)^2$, so the on-resonance excitation rate is inversely proportional to $w(z)$.

Previously,[12] Bordé published a considerably more complex expressions for the two-photon line shape. His analysis considered the interaction with the field to third order, allowed for the two traveling waves to have different frequencies and spatial shapes, and included the second order Doppler effect. The second order Doppler effect results in a shift in the resonant frequency[12] of $-\omega v^2/2c^2$, which for thermal velocities of small molecules in the IR is of the order of tens of Hz, completely negligible compared to the transition time broadening for realistic cavity parameters.

III. LINE SHAPE WITH SATURATION AND AC STARK SHIFT

Analytical expressions are not available in the strong field case but can be computed numerically by integration of the equation of motion $d\vec{r}/dt = -\vec{\Omega} \times \vec{r}$, where $\vec{r} = \left(\mathrm{Re}\,\rho_{gf}, \mathrm{Im}\,\rho_{gf}, \rho_{11} - \rho_{22}\right)$ and $\vec{\Omega} = \left(2\Omega_{2p}e^{-2(b^2+v^2t^2)/w^2}, 0, 2\Delta\omega + \beta\Omega_{2p}e^{-2(b^2+v^2t^2)/w^2}\right)$, where $\beta = \Delta\omega_{fg}/\Omega_{2f}$ (the ratio of the AC Stark Shift in the level separation to the effective two-photon Rabi frequency), which is independent of the field amplitude if the perturbation treatment of nonresonant states is valid. Re ρ_{gf} and Im ρ_{gf} are the real and imaginary parts

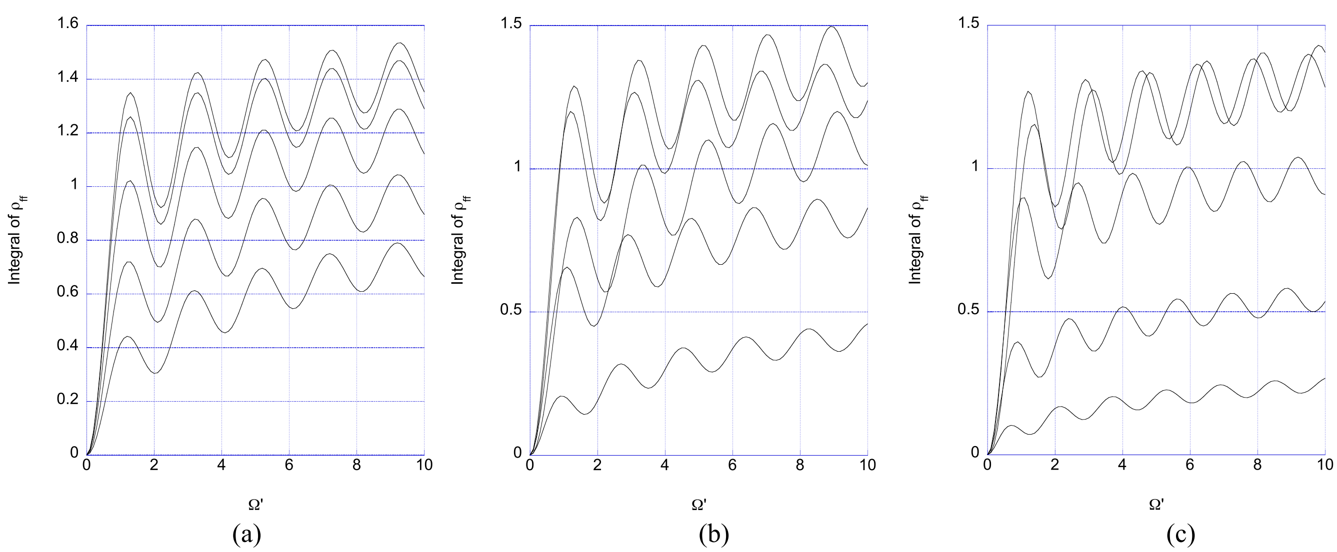

FIG. 1. Plots of excitation probability for a transit-time limited two-photon absorption, integrated over impact parameter *b* and then divided by the optical beam radius, *w*, for normalization. The horizontal axes are the dimensionless Rabi frequency, Ω', as defined in the text. Panel (a) is calculated with no intensity dependence of the transition frequency ($\beta = 0$). The curves, from bottom to top, correspond to dimensionless detuning of $\Delta\omega'$ = 2.0, 1.5, 1.0, 0.5, 0.0. Panel (b) is calculated with the ratio of line shift to Rabi frequency factor $\beta = 1/\sqrt{2}$. The curves (in the order of height of the first peak from bottom to top) are calculated with $\Delta\omega'$ = 2.0, 1.0, −2.0, 0.0, −1.0. The curves in panel (c) are calculated with $\beta = \sqrt{2}$. The curves (in the order of height of the first peak from bottom to top) are calculated with $\Delta\omega'$ = 2.0, 1.0, 0.0, −2.0, −1.0.

of the two-photon coherence, ρ_{gf}. For molecules with perpendicular speed v, $\rho_{ff}(\infty)$ can be written as a function of a dimensionless reduced effective Rabi frequency, $\Omega' = \sqrt{\pi/2}w\Omega_{2p}/v$, and reduced detuning, $\Delta\omega' = 2w\Delta\omega_{gf}/v$. For a molecule passing the center of the optical beam with $\beta = \Delta\omega' = 0$, $\Omega' = 1$ corresponds to a π pulse that inverts the population between states g and f.

Figure 1 shows the integrated (over impact parameter, b) value of $\rho_{ff}(\infty)$ as a function of Ω' divided by w for several values of $\Delta\omega'$ and for three values of $\beta = 0, 1/\sqrt{2}$, and $\sqrt{2}$ shown in three separate panels. For $\beta = 0$, these integrated excitation probability plots are independent of the sign of $\Delta\omega'$. For $\beta > 0$, the curves with negative values of $\Delta\omega'$ have higher peak values, as the negative detuning

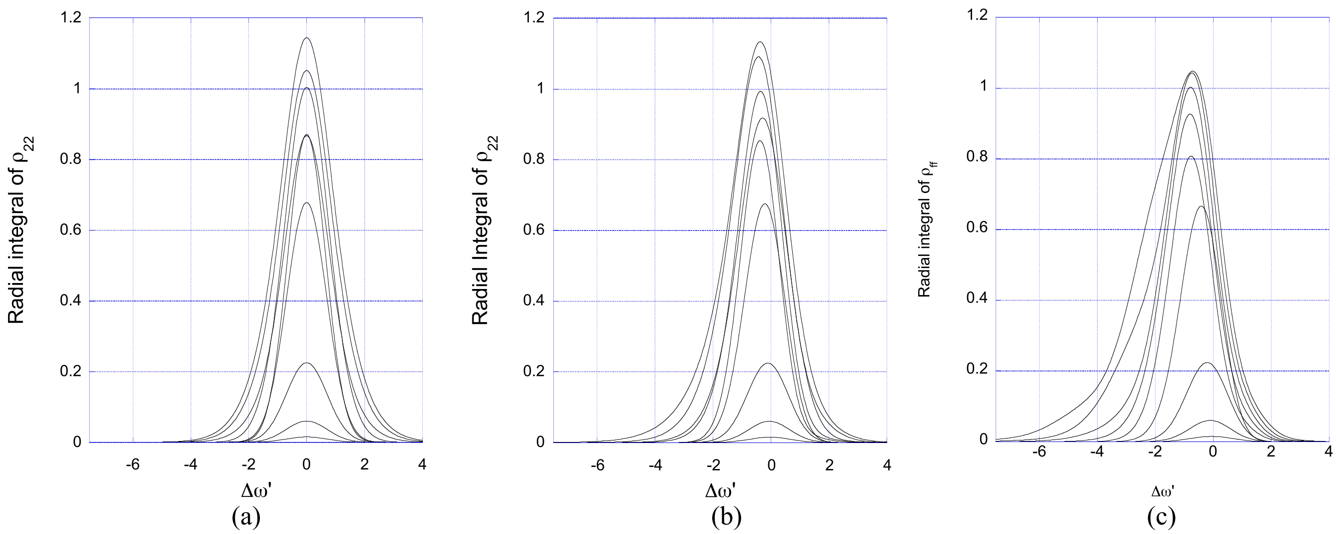

FIG. 2. Plots of excitation probability for a transit-time limited two-photon absorption, integrated over impact parameter b and then divided by the optical beam radius, w, for normalization. The horizontal axis is the dimensionless angular frequency detuning, $\Delta\omega'$, as defined in the text. Panel (a) is calculated with no intensity dependence of the transition frequency (β = 0); curves correspond to the reduced Rabi frequencies of 0.1, 0.2, 0.4, 0.8, 1.6, 6.4, 3.2 12.8, and 25.6 from bottom to top. Panel (b) is calculated with the ratio of line shift to the Rabi frequency factor $\beta = 1/\sqrt{2}$; curves correspond to the reduced Rabi frequencies of 0.1, 0.2, 0.4, 1.6, 0.8, 6.4, 3.2, 12.8, and 25.6 from bottom to top. Panel (c) is calculated with $\beta = \sqrt{2}$; curves correspond to the reduced Rabi frequencies of 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4, 12.8, and 25.6 from bottom to top.

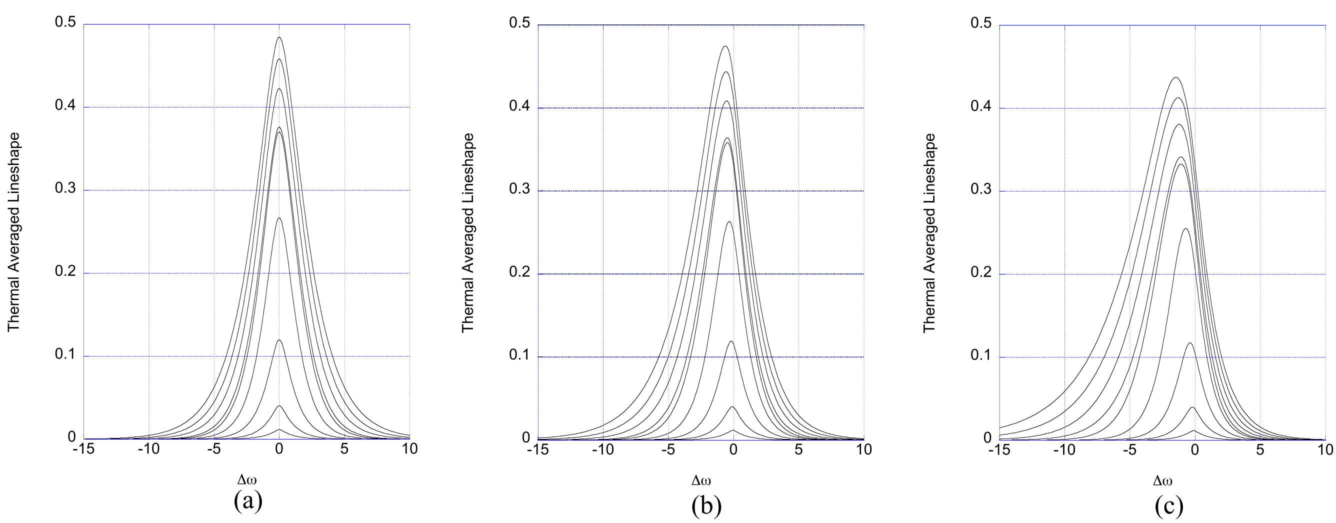

FIG. 3. Plots of thermal averaged two-photon absorption line shapes in the transit-time limit. For each panel, curves correspond to reduced Rabi frequencies of 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4,12.8 and 25.6 from bottom to top. The horizontal axes are the dimensionless angular frequency detuning, $\Delta\omega''$, as defined in the text. Panel (a) is calculated with no intensity dependence of the transition frequency (β = 0). Panel (b) is calculated with the ratio of the line shift to Rabi frequency factor $\beta = 1/\sqrt{2}$, and panel (c) is calculated with $\beta = \sqrt{2}$.

compensates, in part, the light shift near the center of the beam. Figure 2 shows the integrated excitation probability vs $\Delta\omega'$ for values of $\Omega' = 0.1, 0.2, 0.4, 0.8, 1.6, 3.2$, and 6.4 with $\beta = 0, 1/\sqrt{2}$, and $\sqrt{2}$ again shown in separate panels.

Under thermal conditions, the line shape is calculated by averaging the flux of excited molecules leaving the beam. This can be represented by another pair of dimensionless reduced quantities: $\Omega'' = \sqrt{\frac{\pi m}{k_B T}} w\Omega_{2p}$ and $\Delta\omega'' = \sqrt{\frac{2\,m}{k_B T}} w\Delta\omega_{gf}$. Figure 3 shows the calculated line shape, $\sqrt{m/2\,k_B T w^2} \int\int v P(v) \rho_{ff}(\infty, b, v, \Omega_{2p}, \Delta\omega_{gf})\, db\, dv$.

IV. NUMERICAL EXAMPLE

As a numerical example, consider the TPA of NNO (nitrous oxide) pumping the ν_3 vibrational mode, as was recently reported.[13] Here, $m = 44$ u and the mean inverse laser beam radius at the center of the cavity used (mirrors of 1 m radii of curvature, separation of 0.75 m and $\lambda = 4.53$ μm) is $w_0 = 0.90$ mm. At T = 300 K, Eq. (12) predicts a low power transit time limited line shape with a frequency HWHM of 41.2 kHz. The root-mean-squared perpendicular velocity $v_{\rm rms} = \sqrt{2k_B T/m} = 335$ m/s. Saturation intensity, where $\Omega' = 1$, occurs when $\Omega_{2p} = 2.97 \cdot 10^5$ s^{-1}. The detuning of the Q(17) TPA feature is 0.113 cm^{-1} = $2.13 \cdot 10^{10}$ s^{-1}. The spontaneous emission rates for the transitions that make up the near resonant pathway are $A_{ng} = 107$ s^{-1} and $A_{fn} = 205$ s^{-1}, so the approximation $\Omega_{fn} = \sqrt{2}\Omega_{ng}$ is a good one. $\Omega' = 1$ when $\Omega_{ng} = 4.73 \cdot 10^7$ s^{-1}, which occurs for molecules passing through the center of the beam when the on-axis intensity is 56.4 W/cm^2 or a one way optical power of the TEM$_{00}$ equal to 0.717 W. The self-collisional broadening HWHM coefficient for the P(18) line of the fundamental is 0.099 cm^{-1}/bar = 30 kHz/Pa, and the two photon transition should have about the same relaxation rate or a broadening rate of 15 kHz/Pa. Thus, at a NNO pressure of 1 Pa, the pressure broadening width should be about 37% of the transit-time broadening. The published experiment on the TPA of this transition[13] used sample pressures between 100 Pa and 1200 Pa; the sample was air containing 25 ppm of NNO, i.e., NNO partial pressures between 0.1 mPa and 1.2 mPa, approximately three orders of magnitude below that needed to realize the transit-time broadening limit if the sample was pure NNO. Clearly, sensitivity is not the limiting factor in realizing the transit time limited resolution, but it is the stabilization and control of the laser frequency with sufficient resolution (on the order of 1 kHz). That initial experiment used optical feedback locking of the laser to the cavity used for the TPA, which resulted in a frequency jump of the laser the lock was interrupted to observe the cavity intensity ringdown. It should be possible to optically lock the laser to one cavity and observe the TPA in another using an acousto-optic modulator (AOM) as the light attenuator. The small frequency shifts required in the transit time limit could be realized by changes in the RF drive frequency of the AOM, the case in which the laser and cavity it is locked to can be static, which should enhance their frequency stability.

V. CONCLUSIONS

The results of this investigation provide simple expressions for the two-photon absorption line shape in the low pressure limit where collisions while crossing a laser beam can be neglected and the intensity is well below that needed to saturate the two-photon transition. The higher optical intensity case is expressed in dimensionless reduced units for the effective Rabi frequency and light shift and numerical line shape calculations presented for a range of these values.

ACKNOWLEDGMENTS

The author thanks Dr. Gang Zhao, Dr. Adam J. Fleisher, and Dr. Joseph Hodges for numerous discussions on two-photon absorption, including the transit time limit.

DATA AVAILABILITY

The details of the spectra presented in the figures of this paper, along with the program that generated those spectra, are available from the corresponding author upon reasonable request.

REFERENCES

[1] K. K. Lehmann, "Resonance enhanced two-photon cavity ring-down spectroscopy of vibrational overtone bands: A proposal," J. Chem. Phys. **151**, 144201 (2019).
[2] L. S. Vasilenko, V. P. Chebotaev, and A. V. Shishaev, "Line shape of 2-photon absorption in a standing-wave field in a gas," JETP Lett. **12**(3), 113–116 (1970).
[3] B. Cagnac, G. Grynberg, and F. Biraben, "Multiphotonic absorption spectroscopy without Doppler broadening," J. Phys. **34**, 845–858 (1973).
[4] F. Biraben, B. Cagnac, and G. Grynberg, "Experimental evidence of 2-photon transition without Doppler broadening," Phys. Rev. Lett. **32**, 643–645 (1974).
[5] C. Flytzanis, "Theory of nonlinear optical susceptibilities," in *Quantum Electronics: A Treatise*, edited by H. Rabin and C. Tang (Academic Press, New York, 1975), Vol. 1, pp. 9–207.
[6] C. J. Bordé, J. L. Hall, C. V. Kunasz, and D. G. Hummer, "Saturated absorption line shape: Calculation of transit-time broadening by a perturbation approach," Phys. Rev. A **14**, 236–263 (1976).
[7] M. C. Li, "Separated-beam experiments and transit-time broadening," Phys. Rev. A **23**, 2995–3002 (1981).
[8] A. Yariv, *Quantum Electronics*, 2nd ed. (John Wiley & Sons, New York, 1975).
[9] J. H. Shirley, "Solution of Schrödinger equation with a Hamiltonian periodic in time," Phys. Rev. **138**, B979–B987 (1965).
[10] G. Grynberg, "Doppler-free multi-photon excitation: Light shift and saturation," J. Phys. **40**, 657–664 (1979).
[11] P. F. Bernath, *Spectra of Atoms and Molecules* (Oxford University Press, Oxford, 2016), p. 293.
[12] C. Bordé, "Line-shape in Doppler-free 2-photon spectroscopy," C. R. Hebd. Seances Acad. Sci., Ser. B **282**(16), 341–344 (1976).
[13] G. Zhao, D. M. Bailey, A. J. Fleisher, J. T. Hodges, and K. K. Lehmann, "Doppler-free two-photon cavity ring-down spectroscopy of a nitrous oxide (N_2O) vibrational overtone transition," Phys. Rev. A **101**, 144201 (2020).