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Infrared light on molecule-molecule and molecule-surface collisions

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By analyzing measured infrared absorption of pure CH_4 gas under both "free" (large sample cell) and "confined" (inside the pores of a silica xerogel sample) conditions we give a demonstration that molecule-molecule and molecule-surface collisions lead to very different propensity rules for rotational-state changes. Whereas the efficiency of collisions to change the rotational state (observed through the broadening of the absorption lines) decreases with increasing rotational quantum number J for CH_4-CH_4 interactions, CH_4-surface collisions lead to J-independent linewidths. In the former case, some (weak) collisions are inefficient whereas, in the latter case, a single collision is sufficient to remove the molecule from its initial rotational level. Furthermore, although some gas-phase collisions leave J unchanged and only modify the angular momentum orientation and/or symmetry of the level (as observed through the spectral effects of line mixing), this is not the case for the molecule-surface collisions since they always change J (in the studied $J = 0$–14 range).

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The fact that interactions between gas-phase molecules modify their internal states is well known. If efficient enough, such intermolecular "collisions" change the principal rotational quantum number J. Weaker collisions leave J unchanged and only induce population transfers within the sublevels of a given J. These processes have received considerable attention since they probe intermolecular potentials and dynamics, are involved in nonequilibrium gas kinetics, and affect spectra resulting from molecule-light interactions, for instance. Their importance for radiative heat transfer and optical soundings has motivated numerous investigations on the effects of pressure on gas-phase spectra [1]. These studies show that collisions lead to the well-known Lorentz broadening of the spectral lines as they change the rotational state and thus shorten the lifetime of the associated internal levels. The resulting linewidths, proportional to pressure in the binary-collision regime, essentially decrease with increasing J [2,3]. This observation is explained by the fact that as a molecule spins faster it is more difficult to change its rotational state so that only strong (and rare) collisional events are efficient. As collisions induce population exchanges between rotational levels, they lead to transfers of absorption intensity among the various collisionally coupled optical transitions. This "line-mixing" process can strongly affect the spectral shape of manifolds composed of closely spaced lines [1]. In CH_4 absorption, the influence of collisions that leave J unchanged but modify the angular momentum orientation and/or symmetry of the level has been observed in the infrared and modeled [4,5]. It was shown [4] that the contribution of such collisions, relative to those changing J, increases with J.

Understanding scattering, energy exchanges, rotational-state changes, and reaction processes in molecule-surface collisions is interesting for many reasons. These include the soundings of the surface structure and molecule-surface potential as well as catalysis, corrosion, and dissociative chemisorption, for instance (for examples see Refs. [6,7]). Both experiments and calculations (e.g., Refs. [8–12] and those therein) on the scattering of linear molecules by surfaces indicate that very large amounts of angular momentum are transferred to the molecule from the surface. However, most of these studies involve crystal surfaces and conditions very different from thermal equilibrium (high translational energy and rotationally cold molecular beams). To the best of our knowledge little is known concerning J-conserving but rotational-state-changing molecule-surface collisions, in opposition to the situation for gas-phase intermolecular interactions. We found no results for methane despite several studies for this gas (e.g., [13–15]). Furthermore, work is needed that simultaneously investigates and compares the influences of gas-phase molecule-molecule interactions and of molecule-surface collisions. This is of interest since one may expect significant differences between the efficiency and the propensity rules of these two collisional processes, a question that is the subject of the present study.

In this paper, we analyze infrared absorption spectra of methane gas recorded at room temperature under two different conditions. In the first, denoted as "confined," CH_4 is introduced at low pressure within the pores of a silica xerogel sample, which are of a size much smaller than the mean-free path between collisions. The spectra are then dominated by

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the influence of collisions between the molecules and the inner surfaces of the pores. In the second, denoted as "free", CH_4 is enclosed in a cell of dimensions much larger than the mean-free path at near-atmospheric pressures. The absorption shapes then only reflect the effects of CH_4-CH_4 collisions.

For the study of confined (but *not* adsorbed) gases, porous materials are of interest since they enable tight confinement while providing significant optical paths [16,17]. In this study, a silica xerogel sample, made by a sol-gel technique [18], was used. Transmission spectra of CH_4 gas within the pores (of diameter ≈80 nm) of this sample were recorded in the ν_3 band near 3.3 μm as described in Ref. [17]. Spectra obtained for pressures of 9.91 and 31.1 hPa were in excellent agreement. Under these conditions, the mean-free path is greater than 2 μm, much larger than the pore size. The influence of CH_4-CH_4 interactions is thus negligible, and the spectra are governed by the collisions of molecules with the pore inner walls.

For free CH_4, the device described in Ref. [19], which enables short optical paths adapted to the strong absorption in the ν_3 band, was used. Spectra were recorded for pressures between 589 and 790 hPa. These pressures were chosen such that the linewidths are close to those observed for confined CH_4. Under these conditions, the mean-free path is shorter than a fraction of a micron, much smaller than the cell length (≈80 μm). The influence of collisions between the molecules and the cell walls is thus negligible, and the spectra are governed by CH_4-CH_4 interactions.

In both experiments, high-resolution Bruker IFS 120 Fourier-transform spectrometers were used, fitted with a globar source, a KBr beam splitter, and an InSb detector. The maximum optical path difference was set to 225 cm for a spectral resolution of 0.004 cm^{-1}. Transmission spectra were obtained by ratioing recordings made with and without CH_4 gas in the cell or xerogel.

We investigated the R branch ($J \rightarrow J+1$ transitions) of the CH_4 ν_3 band, which is composed [3] of a series of $R(J)$ manifolds, separated by about 10 cm^{-1} and associated with successive values of the lower-level rotational quantum number J. Each manifold contains several closely spaced lines associated with different nuclear spins and symmetries of the lower and upper levels of the transitions and with different angular momentum orientations. The number of lines in each manifold increases with J. Although there is a single $R(1)$ line, the $R(6)$ and $R(10)$ manifolds include 6 and 12 intense transitions, respectively [3]. In the $R(10)$ manifold, eight lines originate from levels of nuclear spin $I = 1$ (orthomethane, states denoted as $F1$ or $F2$), two come from levels with $I = 0$ (paramethane, E states), and the remaining two come from levels with $I = 2$ (metamethane, $A1$ or $A2$ states). Collision-induced transfers of populations occur within each of the sets of levels of a given nuclear spin I with resulting signatures in the absorption spectrum [4,5].

Modeling collisional effects within manifolds requires knowledge of the rate for the depopulation of each individual level and the state-to-state rates connecting the sublevels. In spectroscopic terms, this is taken into account through the "relaxation matrix" W [1] constructed in the line space ("Liouville space"). Within a manifold, the absorption coefficient $\alpha(\omega)$ at angular frequency ω (written neglecting the Doppler effect for simplicity) is given by [1]

$$\alpha(\omega) \propto \mathrm{Im}\left\{\sum_{\ell,\ell'} \rho_\ell d_\ell d_{\ell'} \langle\langle \ell' || [\Omega - \Omega_0 - iW]^{-1} || \ell \rangle\rangle\right\}, \quad (1)$$

with a constant proportionality factor whose value will be adjusted until the measured and calculated absorbances have the same area. The sum in Eq. (1) extends over all lines ℓ and ℓ'; ρ_ℓ and d_ℓ are the relative population of the initial level and the dipole matrix element of line ℓ, respectively. Ω, Ω_0, and W are matrices, and $\langle\langle \ell' || \cdots || \ell \rangle\rangle$ designates a matrix element. Ω and Ω_0 are diagonal, associated with the current angular frequency ω and with the positions ω_ℓ of the individual transitions, respectively. The relaxation matrix W contains all the effects of collisions on the spectral shape. Its off-diagonal elements describe the collisional coupling between absorption lines (line mixing [1]), whereas the diagonal terms are the collisional half-widths at half maximum Γ_ℓ of the individual transitions. Note that Eq. (1) leads to the addition of Lorentzian line profiles if the off-diagonal terms of W are disregarded.

In the simulations, the parameters ω_ℓ, ρ_ℓ, and d_ℓ were taken from the HITRAN spectroscopic database [3]. For the free (f) gas, the values of $\langle\langle \ell || W^f || \ell \rangle\rangle = \Gamma_\ell^f = P\gamma_\ell^f$ for each pressure P were calculated from the pressure-broadening coefficients γ_ℓ^f provided by the same database. The off-diagonal elements of W^f were either set to zero (no collisional exchanges between sublevels of a given J) or derived from calculated state-to-state rates as explained in Refs. [4,5]. For the confined (c) gas, W^c was constructed as follows. Recall that analyses of spectra of several gases confined in the same xerogel sample have shown [17] that the lines are broadened through collisions with the pore walls. Furthermore, the resulting half-widths are independent of the transition and proportional to $M^{-1/2}$ where M is the molecular mass. We thus assumed that the same rule is applicable to CH_4. Using the proportionality factor derived from well-isolated lines of CO, CO_2, and N_2O, equal to 0.184 ± 0.007 cm^{-1} $\mathrm{g}^{1/2}$ [17], we set $\langle\langle \ell || W^c || \ell \rangle\rangle = \Gamma^c = 0.046\ \mathrm{cm}^{-1}$ for all methane lines. As for the free gas, the off-diagonal elements were either set to zero or assumed to be the same, relative to the diagonal term, as for free gas, i.e.,

$$\langle\langle \ell' || W^c || \ell \rangle\rangle = \langle\langle \ell' || W^f || \ell \rangle\rangle \frac{\langle\langle \ell || W^c || \ell \rangle\rangle}{\langle\langle \ell || W^f || \ell \rangle\rangle_{\mathrm{av}}}, \quad (2)$$

where $\langle\langle \cdots \rangle\rangle_{\mathrm{av}}$ denotes an average over the manifold transitions.

Let us emphasize that, with the given models, all parameters influencing the calculated spectral shapes have been determined fully independent of the present experiments. The comparisons between measured and calculated spectra presented below thus provide a meaningful test.

In Fig. 1(a) is plotted a measured spectrum in the R branch of the ν_3 band of free CH_4. In Fig. 1(c) it is compared with the results of calculations disregarding the collision-induced changes in the sublevel symmetry and/or angular momentum orientation. The results obtained when these processes are taken into account are displayed in Fig. 1(e).

These results confirm previous ones [4,5] and show that some CH_4-CH_4 collisions leave J unchanged but induce population transfers among the sublevels within each manifold. Note that the amplitude of the residuals in Fig. 1(c) relative to

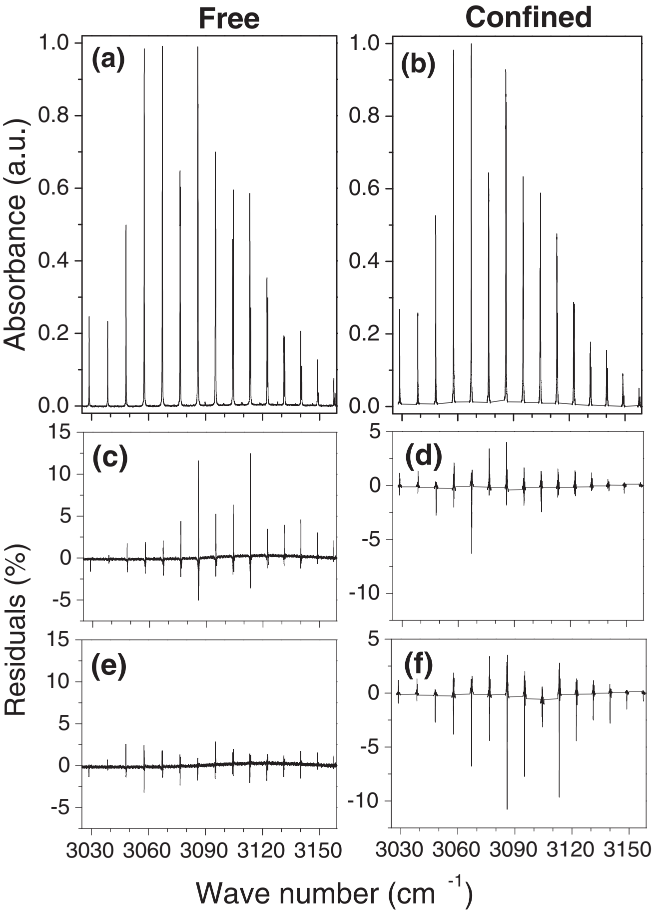

FIG. 1. Top: R-branch absorption of CH_4 measured (a) for the free gas and a pressure of 680 hPa and (b) for the confined gas at 9.91 hPa. The lower panels display differences (magnified by a factor of 100) between measured spectra and those obtained from calculations that disregard [(c) and (d)] or take into account [(e) and (f)] the collisional transfers among the sublevels of each manifold.

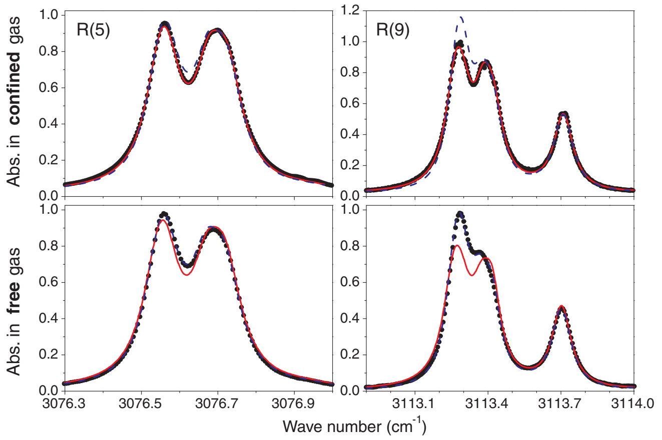

FIG. 2. (Color online) Absorption spectra of the $R(5)$ and $R(9)$ manifolds of CH_4 measured (top) for the confined gas and (bottom) for the free gas. For the free gas, the $R(5)$ and $R(9)$ were measured at 631 and 680 hPa, respectively. The black dots (not all plotted) are measured values whereas the simulations with and without the inclusion of collisional transfers among sublevels are in blue (dahsed line) and red (solid line), respectively.

the absorption at the peak centers in Fig. 1(a) globally increases with J. Indeed, the detailed analysis of $R(J)$ manifolds [4] shows that the relative contribution of J-conserving but state-changing collisions for CH_4 in N_2 increases from a few percent at small J values to nearly 50% for $J = 14$. These data suggest that long-range collisions become inefficient in changing J as the molecule rotates faster but can still induce transfers between sublevels of a given J. For confined methane, a comparison of panels (d) and (f) in Fig. 1 leads to the opposite conclusion. The measured-to-calculated residuals now show that a negligible number of CH_4-surface collisions leave J unchanged while inducing exchanges of population among sublevels. These different behaviors of free and confined methane are confirmed by closer looks at two manifolds plotted in Fig. 2. For the free gas, taking into account J-conserving transfers of populations within the manifold leads to almost perfect agreement with measurements whereas neglecting this process does not and underestimates the peak absorption. For confined gas, the situation is completely reversed.

To further check that the broadening of absorption lines by CH_4-surface collisions is independent of the transition, the confined gas spectrum at 9.91 hPa was adjusted. The fit was made assuming that all lines within each manifold have a Lorentzian profile and the same half-width $\Gamma^c(J)$. The quality of the spectrum fit in Fig. 3(a) validates these two assumptions. The retrieved linewidths are displayed in Fig. 3(b) together with free gas values and with the J-independent broadening deduced from results obtained [17] using absorption by CO, CO_2, and N_2O and the scaling law in $M^{-1/2}$ (see above). As can be seen, the results validate, within uncertainties, the assumption of a fully J-independent broadening (in the $J = 0$–14 range studied) induced by CH_4-surface collisions.

Although temporally trapped or adsorbed molecules on the ill-defined surfaces of the xerogel pores may contribute to the observed spectra of confined methane, we believe this contribution is negligible for several reasons. The first is that experiments are performed at room temperature with pores of diameter of about 80 nm, two conditions not favorable for the adsorption of a significant number of molecules. The second is that the spectrum of adsorbed CH_4 is dominated (e.g., Refs. [20,21]) by strong "Q branches" that result from the dipole induced in the molecule by the static electric field of the surface and which are broad since the lifetime of the coherence of this dipole is short. Such features are not seen in our spectra. Hence, as expected and confirmed by the quality of the spectral fit in Fig. 3(a), the contribution of adsorbed molecules in the $R(J)$ manifold is negligible.

The opposite spectral effects of CH_4-CH_4 and CH_4-surface collisions may be qualitatively explained along the following arguments [11,12]. In most collisions in the gas phase, the molecules pass by each other at distances where the intermolecular potential gradient is relatively small. Such events leave J unchanged since only strong enough collisions can modify J, which are those for small values of the impact parameter and significant relative translational energies (when compared with the rotational energy jumps). In the vibrational ground state of methane, the energy gap between levels J

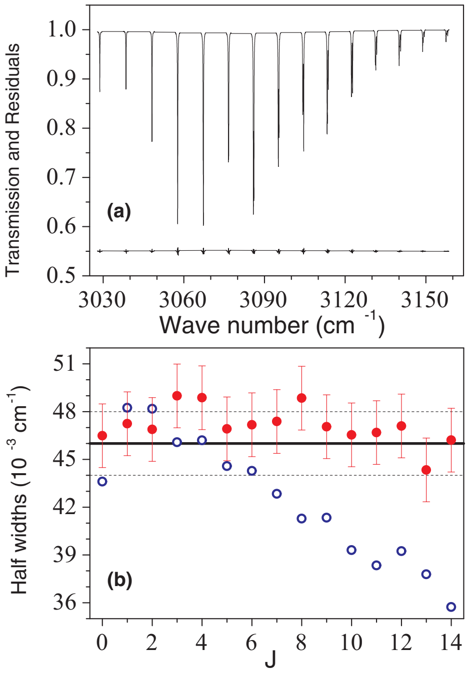

FIG. 3. (Color online) (a) Measured R-branch transmission spectrum of CH_4 confined in the silica xerogel pores at 9.91 hPa and measure-to-fit residuals shifted by +0.55. (b) Half-widths in the $R(J)$ manifolds: The full red circles (with 5% error bars) have been retrieved from the fit of the spectrum in (a); the thick horizontal line is deduced from the half-widths of CO, CO_2, and N_2O gases confined in the same xerogel [17]; the dashed lines defining the confidence interval; the open blue circles are the averaged half-widths [3] of the lines of the $R(J)$ manifolds for the free gas at 600 hPa.

and $J+1$ is about 90, 160, and 230 K for $J=5$, 10, and 15, respectively. As J increases, stronger and stronger intermolecular interactions are thus needed, and the rareness of such collisions in free gas explains the decrease in the resulting linewidths with J shown in Fig. 3(b). Simultaneously, the relative contribution of collisions that only change the symmetry of the level and/or the orientation of the angular momentum increases, explaining the relative increase in the influence of state-changing but J-conserving collisions with J. Conversely, every CH_4-surface collision is, in a sense, a "head-on" collision, similar to a collision at a near-zero impact parameter in a free gas. The molecules are accelerated toward the surface by the attractive well of the CH_4-wall potential before they feel the repulsive front and "bounce away." The repulsive part of the potential being very steep, such collisional events are all strong and extremely efficient in changing J regardless of its value (in the $J=0$–14 range studied). The resulting linewidths are thus transition and J independent and only conditioned by the frequency of molecule-surface collisions [17,22] (i.e., the mean-molecular speed divided by the confinement size). Obviously, as J is always changed, there is no population transfer between sublevels of the same J and thus no line-mixing effects in the $R(J)$ manifolds as demonstrated in this paper.

We believe that the efficiency of a single molecule-surface collision in changing J is a general rule that applies to most molecules under "normal" rotation conditions. This statement is sustained by the fact that the observed linewidths of confined CO, CO_2, and N_2O gases are also independent of J [17], contrary to the case of the free gas [3]. One should nevertheless note that these findings are for J values below 14, 20, 50, and 50 for CH_4, CO, CO_2, and N_2O, respectively. With these upper limits of J, the rotational periods involved are all greater than about 0.3 ps. At this time scale, the translational displacement is typically of 1 to 2 Å at room temperature so that the molecule almost does not rotate while moving in the short-distance interval subjected to the repulsive part of the molecule-surface potential. The molecule thus feels the strong anisotropy of this potential which, in return, induces a change in J. For molecules rotating extremely fast such that many rotations occur at short distances from the surface, the situation would be different. Indeed, as in gas-phase intermolecular collisions [23–25], the interactions of such "superrotors" with surfaces are expected to be much less efficient in changing J. Checking this statement is a difficult task but may be feasible using the optical centrifuge technique [26,27] applied to molecules at low pressure near a surface or to a molecular beam hitting a surface. As shown in Ref. [28] this would also bring interesting information on the scattering of aligned molecules by surfaces.

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[1] J.-M. Hartmann, C. Boulet, and D. Robert, *Collisional Effects on Molecular Spectra: Laboratory Experiments and Models, Consequences for Applications* (Elsevier, Amsterdam, 2008).

[2] T. Gabard and V. Boudon, J. Quant. Spectrosc. Radiat. Transfer **111**, 1328 (2010).

[3] L. S. Rothman, I. E. Gordon, Y. Babikov, A. Barbe, D. C. Benner, P. F. Bernath, M. Birk, L. Bizzocchi, V. Boudon, L. R. Brown, A. Campargue *et al.*, J. Quant. Spectrosc. Radiat. Transfer **130**, 4 (2013).

[4] D. Pieroni, Nguyen-Van-Thanh, C. Brodbeck, C. Claveau, A. Valentin, J.-M. Hartmann, T. Gabard, J.-P. Champion, D. Bermejo, and J.-L. Domenech, J. Chem. Phys. **110**, 7717 (1999).

[5] H. Tran, P.-M. Flaud, T. Gabard, F. Hase, T. von Clarmann, C. Camy-Peyret, S. Payan, and J.-M. Hartmann, J. Quant. Spectrosc. Radiat. Transfer **101**, 284 (2006).

[6] *Atomic and Molecular Beams: State of the Art 2000*, edited by R. Campargue (Springer, Heidelberg, 2001).

[7] R. Diez Muino and H. F. Busnengo, *Dynamics of Gas-Surface Interactions*, Springer Series in Surface Sciences (Springer, Heidelberg, 2013).

[8] H. Ambaye and J. R. Manson, J. Chem. Phys. **125**, 084717 (2006).

[9] C. M. Matthews, F. Balzer, A. J. Hallock, M. D. Ellison, and R. N. Zare, Surf. Sci. **460**, 12 (2000).

[10] K. Golibrzuch, P. R. Shirhatti, I. Rahinov, D. J. Auerbach, A. M. Wodtke and C. Bartels, Phys. Chem. Chem. Phys. **16**, 7602 (2014).

[11] D. J. Kouri and R. B. Gerber, Israel J. Chem. **22**, 321 (1982).

[12] D. E. Fitz, A. O. Bawagan, L. H. Beard, D. J. Kouri, and R. B. Gerber, Chem. Phys. Lett. **80**, 537 (1981).

[13] A. C. Wight and R. E. Miller, J. Chem. Phys. **109**, 1976 (1998).

[14] S. Yagyu, Y. Kino, T. Ikeuchi, T. Hiraoka, T. Kondo, and S. Yamamoto, Jpn. J. Appl. Phys., Part 1 **38**, 6910 (1999).

[15] R. Milot, A. W. Kleyn, and A. P. J. Jansen, J. Chem. Phys. **115**, 3888 (2001).

[16] T. Svensson, E. Adolfsson, M. R. Lewander, C. T. Xu, and S. Svanberg, Phys. Rev. Lett. **107**, 143901 (2011).

[17] J. Vander Auwera, N. H. Ngo, H. El Hamzaoui, B. Capoen, M. Bouazaoui, P. Ausset, C. Boulet, and J.-M. Hartmann, Phys. Rev. A **88**, 042506 (2013).

[18] H. El Hamzaoui, L. Courthéoux, V. Nguyen, E. Berrier, A. Favre, L. Bigot, M. Bouazaoui, and B. Capoen, Mater. Chem. Phys. **121**, 83 (2010).

[19] S. B. Morales, E. Pangui, X. Landsheere, H. Tran, and J.-M. Hartmann, Appl. Opt. **53**, 4117 (2014).

[20] E. Cohen de Lara, J. Soussen, and A.-M. Goulay, Mol. Phys. **96**, 987 (1999).

[21] D. Scarano, S. Bertarione, G. Spoto, A. Zecchina, and C. Otero Arean, Thin Solid Films **400**, 50 (2001).

[22] J.-M. Hartmann, V. Sironneau, C. Boulet, T. Svensson, J. T. Hodges, and C. T. Xu, Phys. Rev. A **87**, 032510 (2013).

[23] A. Korobenko, A. A. Milner, and V. Milner, Phys. Rev. Lett. **112**, 113004 (2014).

[24] L. Yuan, S. W. Teitelbaum, A. Robinson, and A. S. Mullin, Proc. Natl. Acad. Sci. USA **108**, 6872 (2011).

[25] Y. Khodorkovsky, U. Steinitz, J.-M. Hartmann, and I. S. Averbukh, Nature Comm. **6**, 7791 (2015).

[26] J. Karczmarek, J. Wright, P. Corkum, and M. Ivanov, Phys. Rev. Lett. **82**, 3420 (1999).

[27] D. M. Villeneuve, S. A. Aseyev, P. Dietrich, M. Spanner, M. Y. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **85**, 542 (2000).

[28] Y. Khodorkovsky, J. R. Manson, and I. S. Averbukh, Phys. Rev. A **84**, 053420 (2011).