

Four-wave mixing spectroscopy of gas-surface scattering

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A detailed theory of four-wave mixing (FWM) at a gas-solid interface is developed. Geometry of excitation, where two electromagnetic waves propagate perpendicularly to the interface and the third one is evanescent traveling along it, is considered. Assuming that the evanescent wave penetration depth into the gas is much less than the mean free path of gas molecules, it is shown that FWM spectroscopy allows to distinguish between the contributions from gas molecules moving to the surface, desorbed from it and directly scattered into the gas. It is concluded that by scanning the wave frequencies across the molecular transitions it is possible to determine the parameters of the scattering kernel for direct gas-surface scattering and the velocity-dependent sticking probability. A method based on this principle could open opportunity for studying adsorption, desorption and gas-surface scattering dynamics not only under thermodynamically nonequilibrium conditions but as well as in an equilibrium gas phase.

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I. INTRODUCTION

Gas-surface scattering plays a crucial role in processes of heat and mass transfer at a gas-solid interface, energy and momentum exchange between a gas flux and a streamlined surface, in surface chemical reactions. It is therefore of great importance for such diverse applications as heterogeneous catalysis, chemical vapor deposition and aerodynamics. However, investigation of this phenomenon faces a fundamental problem: “in the presence of an equilibrium gas phase, there is no means whatsoever to distinguish between desorbing, reflected, diffracted or inelastically scattered molecules” [1]. Due to this reason, the gas-surface scattering processes are studied mainly with the use of molecular beams under ultra-high-vacuum conditions. In such a case, the surface coverage with an adsorbate is yet sufficiently different from that under a gas atmosphere of high pressure. Although the coverage can be simulated by means of surface cooling, nevertheless the gas-surface scattering dynamics dependent on the surface temperature cannot be investigated by this way. Therefore, strictly speaking, the data obtained with the use of molecular beams are irrelevant to the surface properties which one deals with in various applications.

Recently, a novel laser spectroscopy approach to this problem has been developed. Laser-induced fluorescence spectroscopy employing evanescent waves (EW's) has been demonstrated to be a sensitive tool for studying gas-surface scattering dynamics [2–5]. An EW wave, being strongly spatially localized near the surface, excites only molecules within the Knudsen's layer where the intermolecular collisions are negligible. If in addition the gas is illuminated by a laser beam perpendicular to the surface, it is possible, due to the Doppler effect, to selectively excite either the molecules approaching the surface or the ones departing from it. This opportunity allows one to determine the gas-surface scattering kernel, a fundamental quantity in gas-surface interac-

tions. It has been realized for sodium atoms scattered by a glass surface and the contributions of both the desorbed and directly scattered (i.e., not trapped at the surface) atoms were spectrally distinguished [5]. However, this problem was resolved for thermodynamically nonequilibrium conditions when the gas phase was simulated by a source of sodium atoms and the contribution of the directly scattered atoms could be easily identified. Thus the question still remains: Is it possible to investigate the dynamics of gas-surface scattering in an equilibrium gas phase?

In this paper, we propose for the first time a spectroscopic method based on four-wave mixing (FWM) technique [6] which allows to distinguish between the contributions of molecules arriving at the surface, those desorbed from it and those directly scattered into the gas phase where molecules, although they have induced polarization, are in equilibrium with respect to their external degrees of freedom. We show that by this way it is possible to determine the scattering kernel that provides comprehensive information on gas-surface scattering.

II. EVOLUTION OF A SINGLE MOLECULE

Assume that the ground electronic state of a gas molecule has sublevels $|g\rangle$ and $|g'\rangle$, and the excited electronic state has sublevels $|e\rangle$ and $|e'\rangle$ [7] [Fig. 1(a)]. Let the gas molecules be

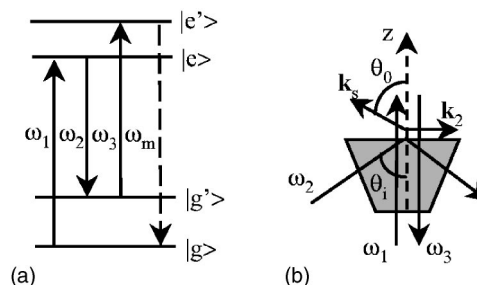


FIG. 1. (a) The excitation scheme of the molecular levels. (b) Geometry of the four-wave mixing process.

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excited by two laser beams of frequencies ω_1 and ω_3 traveling perpendicularly to the gas-solid interface and by an EW of frequency ω_2 propagating along it [Fig. 1(b)]. The laser frequencies are assumed to be in resonance with the molecular transitions as it is shown in Fig. 1(a). The evolution of the molecule density matrix $\rho(\mathbf{r}, \mathbf{v}, t)$ then obeys the Liouville equation

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right)\rho = -\frac{i}{\hbar}[H_0 + V, \rho] - \Gamma\rho, \quad (1)$$

where $\mathbf{r}=(\mathbf{r}_{\parallel}, z)=(x, y, z)$ is the molecule radius-vector, $\mathbf{v}=(\mathbf{v}_{\parallel}, v_z)=(v_x, v_y, v_z)$ is the molecule velocity, H_0 is the Hamiltonian of the molecule in the absence of any external fields, and the operator Γ can be expressed in terms of the relaxation rates γ_{mn} . The operator of interaction between a molecule and the electromagnetic waves, V , can be written in the dipole approximation as follows:

$$V = \sum_{\nu=1,2,3} V_{\nu}, \quad (2)$$

with

$$V_{\nu} = -\frac{1}{2}\boldsymbol{\mu} \cdot \mathbf{E}_{\nu} \exp[-i(\omega_{\nu}t - \mathbf{q}_{\nu} \cdot \mathbf{r})] + \text{c.c.}, \quad (3)$$

where $\boldsymbol{\mu}$ is the dipole moment operator of a molecule, \mathbf{E}_{ν} is the electric field amplitude of the corresponding wave, $\mathbf{q}_{1,3}=(\mathbf{0}, k_{1,3})$ and $\mathbf{q}_2=(\mathbf{k}_2, i\kappa)$ are the wave vectors, and κ^{-1} is the EW penetration depth. We assume that the molecule mean free path exceeds both the EW penetration depth and the mean distance which molecules overcome during the transverse relaxation times γ_{mn}^{-1} . In such a case, it is reasonable to set the boundary conditions for Eq. (1) separately, for the molecules approaching the surface and for the ones departing from it. We shall require the finiteness of the solution for the approaching molecules at infinite distance from the surface, namely [8]

$$|\rho_{mn}^{-}(\mathbf{r}_{\parallel}, z \rightarrow \infty)| < \infty. \quad (4)$$

To specify the boundary conditions for directly scattered molecules, we note that during the flight across the molecule-surface interaction potential, the nondiagonal elements of the molecule density matrix acquire a phase determined by the difference between the molecule-surface potentials in the ground and excited states [9]. For large differences in the adsorption potentials, this phase varies quickly with the incident velocity of a molecule that leads to phase randomization and cancellation of the contribution for molecules departing from the surface [10]. However, as regards the transition between the ground electronic state sublevels $|g\rangle$ and $|g'\rangle$, it is reasonable to assume that this difference is negligible [11] and the coherency $\rho_{g'g}$ can survive during the molecule-surface scattering. In accordance with these arguments, we write the boundary conditions for the nondiagonal matrix elements relevant to our consideration as follows

$$\rho_{mn}^{+}(\mathbf{r}_{\parallel}, z=0) = 0, \quad \text{for } \{mn\} \neq \{g'g\}, \quad (5)$$

$$\rho_{g'g}^{+}(\mathbf{r}_{\parallel}, z=0, \mathbf{v}') = w_{g'g}(\mathbf{v} \rightarrow \mathbf{v}')\rho_{g'g}^{-}(\mathbf{r}_{\parallel}, z=0, \mathbf{v}), \quad (6)$$

where \mathbf{v} and \mathbf{v}' are the velocities of a molecule before and after the scattering, respectively, and we have introduced the probability $w_{g'g}$ that the coherency $\rho_{g'g}$ survives after direct molecule-surface scattering. For molecules trapped at the surface and then desorbed from it, it is reasonable to set $\rho_{g'g}^{+}(\mathbf{r}_{\parallel}, z=0)=0$ and to adopt Eq. (5) for the other matrix elements.

The solving of the problem is simplified if one comes to the Laplace-Fourier transformed quantities

$$\hat{\rho}_{mn}(\mathbf{p}, s) = \int_{z \geq 0} d\mathbf{r} \int_{-\infty}^{\infty} dt \exp(i\mathbf{p} \cdot \mathbf{r} - ist)\rho_{mn}(\mathbf{r}, t), \quad (7)$$

with $\mathbf{p}=(\mathbf{p}_{\parallel}, ip_z)$. The equations for the matrix elements $\hat{\rho}_{mn}(\mathbf{p}, s)$ are obtained from Eq. (1) and have the following form:

$$\begin{aligned} & i(s + \omega_{mn} - \mathbf{p} \cdot \mathbf{v})\hat{\rho}_{mn}(\mathbf{p}, s) - v_z \tilde{\rho}_{mn}(\mathbf{p}_{\parallel}, s) \\ &= -[\Gamma \hat{\rho}(\mathbf{p}, s)]_{mn} - \frac{i}{\hbar} \sum_{k\nu} [(V_{\nu})_{mk} \hat{\rho}_{kn}(\mathbf{p} + \mathbf{q}_{\nu}, s + \omega_{\nu}) \\ & \quad - \hat{\rho}_{mk}(\mathbf{p} + \mathbf{q}_{\nu}, s + \omega_{\nu})(V_{\nu})_{kn} + (V_{\nu})_{mk} \\ & \quad \times \hat{\rho}_{kn}(\mathbf{p} - \mathbf{q}_{\nu}^*, s - \omega_{\nu}) - \hat{\rho}_{mk}(\mathbf{p} - \mathbf{q}_{\nu}^*, s - \omega_{\nu})(V_{\nu})_{kn}], \end{aligned} \quad (8)$$

where

$$\tilde{\rho}_{mn}(\mathbf{p}_{\parallel}, s) = \int d\mathbf{r}_{\parallel} \int_{-\infty}^{\infty} dt \exp(i\mathbf{p}_{\parallel} \cdot \mathbf{r}_{\parallel} - ist)\rho_{mn}(\mathbf{r}_{\parallel}, z=0, t). \quad (9)$$

The boundary conditions (5) and (6) lead to the equations for the transformed quantities

$$\tilde{\rho}_{mn}^{+}(\mathbf{p}_{\parallel}, s) = 0, \quad \text{for } \{mn\} \neq \{g'g\} \quad (10)$$

and

$$\tilde{\rho}_{g'g}^{+}(\mathbf{p}_{\parallel}, s, \mathbf{v}') = w_{g'g}(\mathbf{v} \rightarrow \mathbf{v}')\tilde{\rho}_{g'g}^{-}(\mathbf{p}_{\parallel}, s, \mathbf{v}). \quad (11)$$

III. PERTURBATION THEORY

We assume that the electromagnetic waves do not saturate the relevant transitions, so the solution can be found by expanding both sides of Eq. (8) in power series with respect to the operator V and equating the terms of the same order in V . The boundary conditions (10) and (11) take the form

$$\tilde{\rho}_{mn}^{+(l)}(\mathbf{p}_{\parallel}, s) = 0, \quad \text{for } \{mn\} \neq \{g'g\}, \quad (12)$$

$$\tilde{\rho}_{g'g}^{+(l)}(\mathbf{p}_{\parallel}, s, \mathbf{v}') = w_{g'g}(\mathbf{v} \rightarrow \mathbf{v}')\tilde{\rho}_{g'g}^{-(l)}(\mathbf{p}_{\parallel}, s, \mathbf{v}), \quad (13)$$

where the superscript in parentheses at $\hat{\rho}_{mn}$ denotes the order of the perturbation theory. Now applying the rotating wave approximation [12] one can obtain the solution for $\hat{\rho}_{mn}(\mathbf{p}, s)$ as power series in V , separately for the molecules approaching the surface and departing from it.

A. Zeroth order

We assume that in the absence of external fields only the ground state sublevel $|g\rangle$ is populated among the considered levels and its population is equal to ρ_{gg}^0 . Then one obtains

$$\hat{\rho}_{mn}^{(0)}(\mathbf{p}, s) = \frac{(2\pi)^3}{p_z} \rho_{gg}^0 \delta(\mathbf{p}_{\parallel}) \delta(s) \delta_{mn} \delta_{mg}, \quad (14)$$

with $\delta(x)$ the Dirac's δ function and δ_{ij} the Kronecker's δ symbol, both for molecules moving to the surface and away from it.

B. First order

In the first order the only nonvanishing matrix element is

$$\hat{\rho}_{eg}^{(1)}(\mathbf{p}, s) = \frac{1}{\gamma_{eg} + i(s + \omega_{eg} - \mathbf{p} \cdot \mathbf{v})} \left[v_z \tilde{\rho}_{eg}^{(1)}(\mathbf{p}_{\parallel}, s) + \frac{i}{2} (2\pi)^3 \frac{\Omega_1}{p_z - ik_1} \rho_{gg}^0 \delta(\mathbf{p}_{\parallel}) \delta(s + \omega_1) \right], \quad (15)$$

where the quantity $\tilde{\rho}_{eg}^{(1)}(\mathbf{p}_{\parallel}, s)$ must be determined from the boundary conditions. Here and in the following $\Omega_{\nu} = \boldsymbol{\mu}_{mn} \cdot \mathbf{E}_{\nu} / \hbar$ are the Rabi frequencies of the corresponding transitions. The expression (15) has a pole at

$$p_{z1} = - \frac{\gamma_{eg} + i(s + \omega_{eg} - \mathbf{p}_{\parallel} \cdot \mathbf{v}_{\parallel})}{v_z}. \quad (16)$$

For the molecules moving to the surface $v_z < 0$, and hence $\text{Re}(p_{z1}) > 0$ for any \mathbf{p}_{\parallel} and s . As a result, the corresponding original function is infinite at $z \rightarrow \infty$. To ensure the finiteness of the solution, one has to choose the function $\tilde{\rho}_{eg}^{(1)}(\mathbf{p}_{\parallel}, s)$ so that to cancel the terms containing the pole p_{z1} . The remaining term has the following form:

$$\hat{\rho}_{eg}^{(1)}(\mathbf{p}, s) = \frac{i}{2} (2\pi)^3 \frac{\Omega_1}{p_z - ik_1} A(\mathbf{v}) \rho_{gg}^0 \delta(\mathbf{p}_{\parallel}) \delta(s + \omega_1), \quad (17)$$

where

$$A(\mathbf{v}) = [\gamma_{eg} - i(\Delta_1 - k_1 v_z)]^{-1}, \quad (18)$$

$\Delta_1 = \omega_1 - \omega_{eg}$ is the detuning of the resonance at the $|g\rangle \rightarrow |e\rangle$ transition and we have used the equation $f(x) \delta(x-a) = f(a) \delta(x-a)$.

Taking into account the boundary conditions (12) for scattered molecules, one obtains

$$\hat{\rho}_{eg}^{(1)}(\mathbf{p}, s) = \frac{i}{2} (2\pi)^3 \frac{\Omega_1}{p_z - ik_1} \frac{1}{\gamma_{eg} + p_z v'_z - i\Delta_1} \rho_{gg}^0 \times \delta(\mathbf{p}_{\parallel}) \delta(s + \omega_1). \quad (19)$$

C. Second order

We shall consider only the matrix element $\hat{\rho}_{g'g}^{(2)}$ which is necessary for the calculation of the quantity $\hat{\rho}_{e'g}^{(3)}$ determining the FWM signal. The general solution can be written in the form

$$\hat{\rho}_{g'g}^{(2)}(\mathbf{p}, s) = \frac{1}{\gamma_{g'g} + i(s + \omega_{g'g} - \mathbf{p} \cdot \mathbf{v})} \left[v_z \tilde{\rho}_{g'g}^{(2)}(\mathbf{p}_{\parallel}, s) - \frac{(2\pi)^3}{4} \frac{\Omega_1 \Omega_2 A(\mathbf{v})}{p_z + \kappa - ik_1} \rho_{gg}^0 \delta(\mathbf{p}_{\parallel} - \mathbf{k}_2) \delta(s + \omega_1 - \omega_2) \right]. \quad (20)$$

The denominator in front of the square brackets has a zero at

$$p_{z2} = - \frac{\gamma_{g'g} + i(s + \omega_{g'g} - \mathbf{p}_{\parallel} \cdot \mathbf{v}_{\parallel})}{v_z}. \quad (21)$$

For the molecules moving to the surface this pole leads to the divergence of the original function $\rho_{g'g}^{(2)}$ at $z \rightarrow \infty$. By choosing the quantity $\tilde{\rho}_{g'g}^{(2)}$ in the form

$$\tilde{\rho}_{g'g}^{(2)}(\mathbf{p}_{\parallel}, s) = - \frac{(2\pi)^3}{4} \Omega_1 \Omega_2 A(\mathbf{v}) B(\mathbf{v}) \rho_{gg}^0 \times \delta(\mathbf{p}_{\parallel} - \mathbf{k}_2) \delta(s + \omega_1 - \omega_2), \quad (22)$$

with

$$B(\mathbf{v}) = [\gamma_{g'g} - \kappa v_z - i(\Delta_1 - \Delta_2 - k_1 v_z + \mathbf{k}_2 \cdot \mathbf{v}_{\parallel})]^{-1} \quad (23)$$

and $\Delta_2 = \omega_2 - \omega_{e'g}$, one ensures the finiteness of the solution at infinite distance from the surface. Then we have for arriving molecules

$$\hat{\rho}_{g'g}^{(2)}(\mathbf{p}, s) = - \frac{(2\pi)^3}{4} \frac{\Omega_1 \Omega_2}{p_z + \kappa - ik_1} A(\mathbf{v}) B(\mathbf{v}) \rho_{gg}^0 \times \delta(\mathbf{p}_{\parallel} - \mathbf{k}_2) \delta(s + \omega_1 - \omega_2). \quad (24)$$

The solution for scattered molecules has the form of Eq. (20) where \mathbf{v} must be replaced by \mathbf{v}' and the quantity $\tilde{\rho}_{g'g}^{(2)}$ obeys Eq. (13).

D. Third order

We restrict ourselves by the consideration of the matrix element $\rho_{e'g}^{(3)}$ which determines the radiation at the transition $|g\rangle \rightarrow |e'\rangle$ and hence the intensity of the FWM signal [6]. The general solution for the transformed quantity $\hat{\rho}_{e'g}^{(3)}$ can be written in the form

$$\hat{\rho}_{e'g}^{(3)}(\mathbf{p}, s) = \frac{1}{\gamma_{e'g} + i(s + \omega_{e'g} - \mathbf{p} \cdot \mathbf{v})} \left[v_z \tilde{\rho}_{e'g}^{(3)}(\mathbf{p}_{\parallel}, s) + \frac{i}{2} \Omega_3 \times \hat{\rho}_{g'g}^{(2)}(\mathbf{p} + \mathbf{q}_3, s + \omega_3) \right], \quad (25)$$

where $\hat{\rho}_{g'g}^{(2)}(\mathbf{p}, s)$ is given by Eq. (20). Much as it has been done above, we choose the quantity $\tilde{\rho}_{e'g}^{(3)}$ for molecules moving to the surface so that to ensure the finiteness of the solution at infinite distance from the surface. We then obtain

$$\hat{\rho}_{e'g}^{-(3)}(\mathbf{p}, s) = -i \frac{(2\pi)^3}{8} \Omega_1 \Omega_2 \Omega_3 \rho_{gg}^0 \frac{A(\mathbf{v})B(\mathbf{v})C(\mathbf{v})}{p_z - p_1} \times \delta(\mathbf{p}_{\parallel} - \mathbf{k}_2) \delta(s + \omega_m), \quad (26)$$

where $\omega_m = \omega_1 - \omega_2 + \omega_3$ is the frequency of the radiation resulting from the FWM process and we have introduced the following notations:

$$C(\mathbf{v}) = \{\gamma_{e'g} - \kappa v_z - i[\Delta_m - (k_1 + k_3)v_z + \mathbf{k}_2 \cdot \mathbf{v}_{\parallel}]\}^{-1}, \quad (27)$$

$$p_1 = -\kappa + i(k_1 + k_3), \quad (28)$$

with $\Delta_m = \Delta_1 - \Delta_2 + \Delta_3$ and $\Delta_3 = \omega_3 - \omega_{e'g}$. The contribution of scattered molecules can be written in the form

$$\hat{\rho}_{e'g}^{+(3)}(\mathbf{p}, s) = -i \frac{(2\pi)^3}{8} \Omega_1 \Omega_2 \Omega_3 \rho_{gg}^0 \left[w_{g'g}(\mathbf{v} \rightarrow \mathbf{v}') v'_z A(\mathbf{v}) B(\mathbf{v}) + \frac{A(\mathbf{v}')}{p_z - p_1} \right] \frac{\delta(\mathbf{p}_{\parallel} - \mathbf{k}_2) \delta(s + \omega_m)}{v_z'^2 [p_z - p_2(\mathbf{v}')] [p_z - p_3(\mathbf{v}')]}, \quad (29)$$

where

$$p_2(\mathbf{v}) = -\frac{\gamma_{e'g} - i(\Delta_m + \mathbf{k}_2 \cdot \mathbf{v}_{\parallel})}{v_z} \quad (30)$$

and

$$p_3(\mathbf{v}) = -\frac{\gamma_{g'g} - i(\Delta_1 - \Delta_2 + \mathbf{k}_2 \cdot \mathbf{v}_{\parallel} + k_3 v_z)}{v_z}. \quad (31)$$

IV. SIGNAL FROM AN ENSEMBLE OF MOLECULES

A. General expression for the signal

The intensity of the FWM signal from an ensemble of molecules can be written as follows:

$$I_{FWM} = \frac{c}{2\pi} \langle \mathbf{E}^{(-)}(\mathbf{R}, t) \cdot \mathbf{E}^{(+)}(\mathbf{R}, t) \rangle, \quad (32)$$

where $\mathbf{E}^{(\pm)}$ are the positive- and negative-frequency components of the FWM electric field at the detector, c is the speed of light, \mathbf{R} is the radius vector directed to the observation point and the angular brackets denote the ensemble averaging. The quantities $\mathbf{E}^{(\pm)}$ for a rarefied gas are results of summation over all N molecules participating in the FWM process. In the case when $N^2 \gg N$ the average in Eq. (32) can be approximately factorized and the signal takes the form [13]

$$I_{FWM} \approx \frac{c}{2\pi} \left| \sum_n \langle \mathbf{E}_n^{(+)}(\mathbf{R}, t) \rangle \right|^2, \quad (33)$$

where the contribution from the n th molecule is determined in the dipole approximation by the equation [14]

$$\langle \mathbf{E}_n^{(+)}(\mathbf{R}, t) \rangle = -\frac{\omega_m^2}{c^2 R} \{ [\hat{\boldsymbol{\mu}}_{ge'} \times \hat{\mathbf{R}}] \times \hat{\mathbf{R}} \} \rho_{e'g}^{(3)}(\mathbf{r}_n, t), \quad (34)$$

with $\hat{\boldsymbol{\mu}}_{ge'}$ the lowering part of the dipole moment operator at the transition $|g\rangle \rightarrow |e'\rangle$ and $\hat{\mathbf{R}}$ the unit vector along the vector \mathbf{R} .

The matrix elements which contribute to $\rho_{e'g}^{(3)}$ have a temporal dependence $\sim \exp(-i\omega_m t)$. Then account of the retardation effect is reduced to the substitution

$$t \rightarrow t' = t - \frac{|\mathbf{R} - \mathbf{r}_n|}{c} \approx t - \frac{R - \hat{\mathbf{R}} \cdot \mathbf{r}_n}{c}, \quad (35)$$

the approximation in Eq. (35) being valid in the far zone where $R \gg r_n$. As a result, the matrix element $\rho_{e'g}^{(3)}$ acquires an additional phase factor $\exp[i(\omega_m/c)(R - \hat{\mathbf{R}} \cdot \mathbf{r}_n)]$. Transforming the sum over n into an integral over the gas volume V illuminated by three waves along with the averaging over molecular velocities, we obtain

$$\begin{aligned} \sum_n \langle \mathbf{E}_n^{(+)}(\mathbf{R}, t) \rangle &= -\frac{\omega_m^2}{c^2 R} \exp(ik_s R) \int_{z \geq 0} d\mathbf{r} \\ &\times \{ [\mathbf{P}^{(3)}(\mathbf{r}, t) \times \hat{\mathbf{R}}] \times \hat{\mathbf{R}} \} \exp(-i\mathbf{k}_s \cdot \mathbf{r}) \\ &= -\frac{1}{2\pi} \frac{\omega_m^2}{c^2 R} \exp(ik_s R) \int_{-\infty}^{\infty} ds \\ &\times \{ [\hat{\mathbf{P}}^{(3)}(-\mathbf{k}_s, s) \times \hat{\mathbf{R}}] \times \hat{\mathbf{R}} \} \exp(ist), \end{aligned} \quad (36)$$

where

$$\mathbf{P}^{(3)}(\mathbf{r}, t) = \frac{N}{V} \langle \text{Tr}[\hat{\rho}^{(3)}(\mathbf{r}, t) \hat{\boldsymbol{\mu}}_{ge'}] \rangle_v \quad (37)$$

is the positive frequency part of the nonlinear gas polarization, $\mathbf{k}_s = (\mathbf{k}_{s\parallel}, k_{sz}) = (\omega_m/c) \hat{\mathbf{R}}$ is the wave vector of the generated wave, the angular brackets with the subscript v mean an average over molecular velocities and we have assumed that the linear dimensions of V are much larger than the laser wavelengths. The Laplace-Fourier transformed polarization $\hat{\mathbf{P}}^{(3)}$ can be written as follows

$$\begin{aligned} \hat{\mathbf{P}}^{(3)}(-\mathbf{k}_s, s) &= \frac{N}{V} \langle \text{Tr}[\hat{\rho}^{(3)}(-\mathbf{k}_s, s) \hat{\boldsymbol{\mu}}_{ge'}] \rangle_v \\ &= \hat{X} : \mathbf{E}_1 \mathbf{E}_2^* \mathbf{E}_3 \delta(\mathbf{k}_{s\parallel} + \mathbf{k}_2) \delta(s + \omega_m), \end{aligned} \quad (38)$$

where the tensor \hat{X} has the form [15]

$$(\hat{X})_{ijkl} = \frac{N}{\hbar^3 V} \rho_{gg}^0 (\boldsymbol{\mu}_{ge'})_i (\boldsymbol{\mu}_{e'g'})_j (\boldsymbol{\mu}_{g'e})_k (\boldsymbol{\mu}_{eg})_l (H^- + H^{+d} + H^{+s}). \quad (39)$$

Here the quantities H^- , H^{+d} and H^{+s} determine the contributions to the nonlinear polarization originating from molecules arriving at the surface, those desorbed and those directly scattered, respectively.

The function $\delta(\mathbf{k}_{s\parallel} + \mathbf{k}_2)$ in Eq. (38) implies the phase-matching condition for the FWM process providing its maximum efficiency: $\mathbf{k}_{s\parallel} = -\mathbf{k}_2$. In the case when EW is excited in total internal reflection at a prism surface the direction of phase matching is fixed by the angle θ_0 satisfying the equation

$$\sin \theta_0 = -\frac{\omega_2 \sin \theta_i}{\omega_m \sin \theta_c}, \quad (40)$$

with θ_i the incidence angle of the laser beam exciting EW and θ_c the critical angle for total internal reflection [see Fig. 1(b)]. If the absolute value of the right-hand side of Eq. (40) exceeds unity, the wave generated in the FWM process is evanescent. Assuming that $|\omega_i - \omega_j| \ll \omega_i$ and $\theta_i \approx \theta_c$, we get $\theta_0 \approx -\pi/2$, i.e., the wave of nonlinear polarization propagates in the backscattering direction relatively EW. In such a case $|k_{sz}| \ll k_i$.

To obtain the FWM power at the detector one has to integrate Eq. (33) over the square of the detector surface. That is reduced to the integration over the solid angle $do = \sin \theta d\theta d\varphi$ with θ and φ the spherical coordinates of the vector $\hat{\mathbf{R}}$. The corresponding integrand contains $[\delta(\mathbf{k}_{s\parallel} + \mathbf{k}_2)]^2$. One of the δ functions can be used to remove the integral over do whereas the other one gives $A/(2\pi)^2$ with A the square of the prism surface illuminated by three waves. Finally, one obtains

$$P_{FWM} = \int I_{FWM} R^2 do = \frac{Ak_s^2 c \sin^2 \theta_p}{32\pi^5 \cos \theta_0} |\hat{X} : \mathbf{E}_1 \mathbf{E}_2^* \mathbf{E}_3|^2, \quad (41)$$

where θ_p is the angle between the vectors $\mathbf{P}^{(3)}$ and $\hat{\mathbf{R}}$.

B. Averaging over velocities

As it follows from Eq. (38), the FWM signal is determined by the averaging of the quantity $\hat{\rho}_{e'g}^{(3)}$ over molecular velocities. In a general case when the gas is not in equilibrium with the surface, the fluxes of molecules to the surface and away from it are characterized by different velocity distribution functions, $f^-(\mathbf{v})$ and $f^+(\mathbf{v})$, respectively. The relation between them can be expressed in terms of the scattering kernel $R(\mathbf{v} \rightarrow \mathbf{v}')$ as follows [16,17]:

$$f_f^+(\mathbf{v}') = \int R(\mathbf{v} \rightarrow \mathbf{v}') f_f^-(\mathbf{v}) d\mathbf{v}, \quad (42)$$

where we have introduced the velocity distribution functions normalized to a unit probability flux

$$f_f^\pm(\mathbf{v}) = \frac{|v_z| f^\pm(\mathbf{v})}{\int |v_z| f^\pm(\mathbf{v}) d\mathbf{v}}. \quad (43)$$

The integral in Eq. (43) is taken over $v_z < 0$ for arriving molecules and over $v_z > 0$ for departing ones. The quantity $R(\mathbf{v} \rightarrow \mathbf{v}')$ is defined as the probability density that a molecule striking the surface with velocity between \mathbf{v} and $\mathbf{v} + d\mathbf{v}$ will be scattered at the surface with velocity between \mathbf{v}' and $\mathbf{v}' + d\mathbf{v}'$. In accordance with the two different scattering

channels the scattering kernel can be decomposed by two parts [5],

$$R(\mathbf{v} \rightarrow \mathbf{v}') = R_{des}(\mathbf{v} \rightarrow \mathbf{v}') + R_{dir}(\mathbf{v} \rightarrow \mathbf{v}'), \quad (44)$$

where the kernel

$$R_{des}(\mathbf{v} \rightarrow \mathbf{v}') = S(\mathbf{v}) f_f^{+d}(\mathbf{v}') \quad (45)$$

corresponds to the molecules which were trapped on the surface with the sticking probability $S(\mathbf{v})$ and then desorbed with the velocity distribution f_f^{+d} . The kernel $R_{dir}(\mathbf{v} \rightarrow \mathbf{v}')$ normalized by the condition

$$\int R_{dir}(\mathbf{v} \rightarrow \mathbf{v}') d\mathbf{v}' = 1 - S(\mathbf{v}) \quad (46)$$

describes direct scattering.

Now the averaging of the contributions from different groups of molecules can be written as follows

$$\langle \hat{\rho}_{e'g}^{-s(3)} \rangle_v = \int_{v_z \leq 0} \hat{\rho}_{e'g}^{-s(3)}(\mathbf{v}) f^-(\mathbf{v}) d\mathbf{v}, \quad (47)$$

$$\begin{aligned} \langle \hat{\rho}_{e'g}^{+s(3)} \rangle_v &= \int \int \hat{\rho}_{e'g}^{+s(3)}(\mathbf{v}, \mathbf{v}') R(\mathbf{v} \rightarrow \mathbf{v}') f_f^-(\mathbf{v}) d\mathbf{v} d\mathbf{v}' \\ &= S_T \int \hat{\rho}_{e'g}^{+d(3)}(\mathbf{v}') f_f^{+d}(\mathbf{v}') d\mathbf{v}' + \int \int \hat{\rho}_{e'g}^{+s(3)}(\mathbf{v}, \mathbf{v}') \\ &\quad \times R_{dir}(\mathbf{v} \rightarrow \mathbf{v}') f_f^-(\mathbf{v}) d\mathbf{v} d\mathbf{v}', \end{aligned} \quad (48)$$

where $\hat{\rho}_{e'g}^{+d(3)}$ and $\hat{\rho}_{e'g}^{+s(3)}$ describe the contributions of desorbed and directly scattered molecules and are given by Eq. (29) with $w_{g'g} = 0$ and $w_{g'g} \neq 0$, respectively, and

$$S_T = \int S(\mathbf{v}) f_f^-(\mathbf{v}) d\mathbf{v} \quad (49)$$

is the average sticking probability.

In the following, we shall analyze the case of an equilibrium between a gas and a solid when both f_f^- and f_f^+ are the Maxwellian distribution functions, f_{fM} , characterized by a common temperature T . We shall restrict ourselves by the consideration of the Doppler limit where the Doppler width ω_D is much larger than all the linewidths γ_{mn} as well as the transit-time broadening κv_T with v_T the most probable molecule velocity. Then the integration over velocities in Eqs. (47) and (48) can be carried out analytically. As a result, we obtain for the molecules arriving at the surface and desorbed from it (see Appendix A for the details)

$$\begin{aligned} H &\approx -\frac{2\pi^{7/2}(\gamma_{e'g} - \gamma_{g'g})\Theta(-\Delta_1)\Theta(\Delta_3)\Theta(-k_3)}{k_2^2 v_T^2 [\kappa - i(k_1 + k_3 - k_{sz})]} \\ &\quad \times \{k_3 \Delta_1 - k_1 \Delta_3 + i[k_3 \gamma_{eg} - k_1(\gamma_{e'g} - \gamma_{g'g})]\}^{-1} \\ &\quad \times \exp\left(-\frac{\Delta_1^2}{k_1^2 v_T^2}\right) \left[\frac{dZ(v/v_T)}{dv} \right]_{v=\Delta_2/k_2} \end{aligned} \quad (50)$$

and

$$\begin{aligned}
H^{+d} \approx & -\frac{4\pi^4 S_T \Delta_1 (\gamma_{e'g} - \gamma_{g'g}) \Theta(\Delta_1) \Theta(-\Delta_3) \Theta(-k_3)}{k_1 k_2^2 v_T^3 [\kappa - i(k_1 + k_3 - k_{sz})]} \\
& \times \{k_3 \Delta_1 - k_1 \Delta_3 + i[k_3 \gamma_{eg} - k_1 (\gamma_{e'g} - \gamma_{g'g})]\}^{-1} \\
& \times \exp\left(-\frac{\Delta_1^2}{k_1^2 v_T^2}\right) \left[\frac{dZ(v/v_T)}{dv}\right]_{v=-\Delta_m/k_2}, \quad (51)
\end{aligned}$$

respectively, with $Z(x)$ the plasma dispersion function [18] and $\Theta(x)$ the unit step function.

The contribution from directly scattered molecules (29) includes two terms in the square brackets. The second of them has the same form as the contribution of desorbed molecules. It does not depend on \mathbf{v} and hence the integration over \mathbf{v} can be carried out explicitly. It is reduced to the integral

$$\int R_{dir}(\mathbf{v} \rightarrow \mathbf{v}') f_{fM}(v) d\mathbf{v} = (1 - S_T) f_{fM}(v'). \quad (52)$$

As a result, the contribution of the second term in Eq. (29) to the spectrum has the form of Eq. (51) with S_T replaced by $1 - S_T$.

The averaging over velocities of the first term in Eq. (29) can be carried out by means of successive integrations over \mathbf{v} and \mathbf{v}' . We note that if the molecule-surface potential well depth is much greater than the molecule incident kinetic energy, one can assume that the change in the molecule momentum parallel the surface during scattering is small [19]. In such a case, the scattering kernel can be written in the form

$$R_{dir}(\mathbf{v} \rightarrow \mathbf{v}') = R_{dir}^z(v_z \rightarrow v'_z) \delta(\mathbf{v}'_{\parallel} - \mathbf{v}_{\parallel}), \quad (53)$$

where the reduced scattering kernel R_{dir}^z is normalized by the condition

$$\int_0^{\infty} R_{dir}^z(v_z \rightarrow v'_z) dv'_z = 1 - S(v_z). \quad (54)$$

Under the same assumption, it is reasonable to consider the quantity $w_{g'g}$ as independent on the velocities \mathbf{v} and \mathbf{v}' because the time of flight across the molecule-surface potential depends only slightly on the initial and final velocities far from the surface. Then the result of the integration of Eq. (29) over velocities can be written as follows (see Appendix B for the details):

$$\begin{aligned}
H^{+s} \approx & \frac{1 - S_T}{S_T} H^{+d} - \frac{4i\pi^4 w_{g'g}}{k_1 k_2^2 k_3 v_T^3} J(\Delta_1) \\
& \times \frac{(\gamma_{e'g} - \gamma_{g'g}) \Theta(-\Delta_1) \Theta(\Delta_3) \Theta(k_3)}{\Delta_1 + \Delta_3 + i(\gamma_{eg} + \gamma_{e'g} - \gamma_{g'g})} \left(\frac{\Delta_1}{k_1}\right) \\
& \times \exp\left(-\frac{\Delta_1^2}{k_1^2 v_T^2}\right) \left[\frac{dZ(v/v_T)}{dv}\right]_{v=\Delta_2/k_2}, \quad (55)
\end{aligned}$$

where

$$J(\Delta_1) = \int_0^{\infty} \frac{R_{dir}^z(\Delta_1/k_1 \rightarrow v'_z) v'_z dv'_z}{v'_z + (\Delta_1/k_3) - i\alpha} \quad (56)$$

and α is an infinitesimally small positive quantity. The integral (56) can be evaluated using Eq. (A6).

V. RESULTS AND DISCUSSION

The distinct resonance conditions for different groups of molecules which follow from the Doppler effect allow to distinguish between their contributions. This can be seen from the analysis of Eqs. (50), (51), and (55). In fact, let us consider the following cases.

(i) Both k_3 and Δ_1 are negative and Δ_3 is positive. Then the contribution from the molecules moving from the surface is negligible due to the Θ functions and only the molecules arriving at the surface contribute resonantly to the FWM spectrum.

(ii) Both k_3 and Δ_3 are negative and Δ_1 is positive. Then, analogously, both the contribution of the molecules moving to the surface and that of the second term in H^{+s} are nonresonant. The FWM signal is determined by the function H^{+d} describing the desorbed molecules.

(iii) Both k_3 and Δ_3 are positive whereas Δ_1 is negative. Then only the directly scattered molecules give a resonant contribution determined by the second term in H^{+s} .

Let us consider the latter case in detail. As it follows from Eq. (55), the nonlinear polarization in this case is determined by the scattering kernel for direct scattering taken at the initial velocity dictated by the detuning of wave 1. It is worthwhile to normalize the FWM power obtained in the case (iii) to that in the case (i). When scanning the detuning Δ_3 both signals have sharp maxima, at $\Delta_3 = -\Delta_1$ and at $\Delta_3/k_3 = \Delta_1/k_1$, respectively. Let us normalize the maximal power obtained in the case (iii) to that obtained in the case (i). The so defined FWM signal has the following form:

$$\begin{aligned}
\eta(\Delta_1) &= \frac{P_{FWM}(\text{case(iii)})}{P_{FWM}(\text{case(i)})} \\
&\approx 4\pi \left(\frac{w_{g'g} \Delta_1}{k_1^2 k_3 v_T}\right)^2 |J(\Delta_1)|^2 |\kappa \\
&\quad - i(k_1 - |k_3| - k_{sz})|^2 \\
&\quad \times \left[\frac{|k_3| \gamma_{eg} + k_1 (\gamma_{e'g} - \gamma_{g'g})}{\gamma_{eg} + \gamma_{e'g} - \gamma_{g'g}}\right]^2. \quad (57)
\end{aligned}$$

As it follows from here, by scanning the detuning Δ_1 it is possible to determine $|J(\Delta_1)|$ provided that the other quantities entering Eq. (57) are known. Basing on an appropriate model, one can then find the parameters of the scattering kernel from a fitting procedure. On the other hand, if the experimental set up allows to measure not only the absolute value of the tensor \hat{X} component but also its phase [20], it is possible to determine the scattering kernel *without any pre-defined analytical form*, using the relation

$$\text{Im}[J(\Delta_1)] = -\pi \frac{\Delta_1}{k_3} R_{dir}^z\left(\frac{\Delta_1}{k_1} \rightarrow -\frac{\Delta_1}{k_3}\right). \quad (58)$$

The knowledge of the function $R_{dir}^z(v_z \rightarrow v'_z)$ gives opportunity to calculate the velocity-dependent sticking probability from Eq. (54). The transfer energy ϵ for which the scattering kernel can be determined is found from the equation

$$\epsilon = \frac{m\Delta_1^2}{2k_1^2} \left[\left(\frac{k_1}{k_3} \right)^2 - 1 \right], \quad (59)$$

with m the mass of a molecule. Assuming that molecules are excited within the Doppler-broadened absorption line we conclude that R_{dir}^z can be probed in the range $\epsilon \leq [(k_1/k_3)^2 - 1]E_T$, where E_T is the most probable kinetic energy of gas molecules.

One additional remark is necessary. When deriving Eq. (51) describing the contribution of desorbed molecules we assumed that their velocity distribution function is a Maxwellian one normalized to a unit probability flux that implies the validity of the Knudsen's cosine law. However this may be not the case for some gas-surface systems [21]. In such a case, the velocity distribution function of desorbed molecules can be determined from the analysis of the FWM signal measured in the configuration (ii).

Further we shall calculate an expected FWM spectrum in the framework of a semiclassical model for direct inelastic gas-surface scattering [19]. It is assumed that the molecule momentum and energy after scattering differ from their initial values as the result of creation or annihilation of a substrate phonon with momentum \mathbf{Q} and energy ϵ . These quantities are related with initial and final molecule velocities by means of the momentum and energy conservation laws. The probability $N(\epsilon, \mathbf{Q})$ of such a process can be represented as

$$N(\epsilon, \mathbf{Q}) = \frac{1}{\pi^{3/2} \Delta \epsilon \Delta K^2} \exp \left[-\frac{(\epsilon - \delta)^2}{\Delta \epsilon^2} \right] \exp \left(-\frac{Q^2}{\Delta K^2} \right), \quad (60)$$

with $\Delta \epsilon = 2\sqrt{k_B T \delta}$, k_B the Boltzmann constant, $\Delta K = \Delta \epsilon / (\sqrt{2}v_R)$ and v_R the Rayleigh mode velocity. The quantity δ is the mean energy transfer which can be considered as an empirical parameter. The direct scattering kernel describes the same process and can be written in the form

$$R_{dir}(\mathbf{v} \rightarrow \mathbf{v}') = CN(\epsilon, \mathbf{Q}), \quad (61)$$

where C is a constant to be determined from the normalization condition. If the quantity ΔK tends to zero, the Gaussian in momentum gives $\delta(\mathbf{Q}) = (1/m^2) \delta(\mathbf{v}'_{\parallel} - \mathbf{v}_{\parallel})$ and we come to Eq. (53) where

$$R_{dir}^z(v_z \rightarrow v'_z) = C \frac{mv'_z}{\sqrt{\pi \Delta \epsilon}} \exp \left\{ -\frac{1}{\Delta \epsilon^2} \left[\frac{m}{2}(v_z'^2 - v_z^2) - \delta \right]^2 \right\}. \quad (62)$$

The factor mv'_z in Eq. (62) arises from the Jacobian of the transformation from the variable ϵ to v'_z . Then the constant C must be determined from the equation

$$\int_{-\infty}^{\infty} \int_0^{\infty} R_{dir}^z(v_z \rightarrow v'_z) f_{fM}(v_z) dv_z dv'_z = 1 - S_T. \quad (63)$$

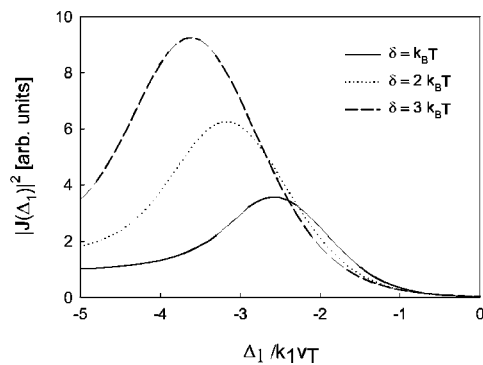


FIG. 2. The value of $|J(\Delta_1)|^2$ calculated assuming the scattering kernel in the Brako-Newns model [19] for different values of the mean energy transfer δ . $k_1/k_3 = 1.2$.

Figure 2 presents the quantity $|J(\Delta_1)|^2$ which determines the normalized FWM signal $\eta(\Delta_1)$ calculated for different values of δ . The function $|J(\Delta_1)|^2$ has a single maximum whose position markedly depends on δ .

Finally, let us estimate the magnitude of the FWM signal. We assume the following typical values of parameters for electronic molecular transitions: $k_p v_T \sim 1$ GHz, $\gamma_{mn} \sim 10$ MHz, $\mu_{mn} \sim 0.1$ D and $\rho_{gg}^0 \sim 10^{-3}$. Taking also $N/V \sim 10^{15}$ cm $^{-3}$ [22], $w_{g'g} \sim 0.1$ [23] and $R_{dir} \sim v_T^{-1} \sim 10^{-4}$ cm $^{-1}$ s [24], we obtain for the contribution of directly scattered molecules $|\hat{X}| \sim 10^{-13}$ cgs. For $A \sim 0.2$ cm 2 and $E_1 \sim E_2 \sim E_3 \sim 1$ cgs, that corresponds to the power density of ~ 100 W/cm 2 , we get that the photon flux in the FWM wave is of the order of 10^3 photons/s that is large enough for experimental observation.

VI. CONCLUSION

In the present paper we have developed a theory of four-wave mixing in a gas boundary layer confined by the EW penetration depth. We have considered the limit where the mean free path of gas molecules exceeds this quantity that ensures a collisionless regime of the molecular flow within the boundary layer. Due to the Doppler effect, one can then excite either the molecules arriving at the surface, or the ones leaving it. In addition, the excitation of both arriving and departing molecules simultaneously by the two different waves propagating perpendicularly to the surface allows to spectrally select the direct scattering channel. The parameters of the direct gas-surface scattering kernel can be extracted from the FWM spectra measured in such a configuration. The integral of this kernel over final velocity, Eq. (54), gives the velocity-dependent sticking probability.

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APPENDIX A: CONTRIBUTION OF ARRIVING MOLECULES

The contribution of the molecules arriving at the surface to the FWM signal is determined by Eq. (26) taken at \mathbf{p}

$=-\mathbf{k}_s$. We represent the product $A(\mathbf{v})B(\mathbf{v})C(\mathbf{v})$ in the following form:

$$A(\mathbf{v})B(\mathbf{v})C(\mathbf{v}) = \frac{i}{k_1 k_2 k_3 (v_{z1} - v_{z2})} \left(\frac{1}{v_z - v_{z1}} - \frac{1}{v_z - v_{z2}} \right) \times \left[\frac{1}{v_x - v_{x1}(v_z)} - \frac{1}{v_x - v_{x2}(v_z)} \right], \quad (\text{A1})$$

where

$$v_{x1}(v_z) = \frac{1}{k_2} [\Delta_2 - \Delta_1 + k_1 v_z - i(\gamma_{g'g} - \kappa v_z)], \quad (\text{A2})$$

$$v_{x2}(v_z) = \frac{1}{k_2} [-\Delta_m + (k_1 + k_3)v_z - i(\gamma_{e'g} - \kappa v_z)], \quad (\text{A3})$$

$$v_{z1} = \frac{1}{k_1} (\Delta_1 + i\gamma_{eg}), \quad (\text{A4})$$

$$v_{z2} = \frac{1}{k_3} [\Delta_3 + i(\gamma_{e'g} - \gamma_{g'g})] \quad (\text{A5})$$

and we have chosen the x axis along the \mathbf{k}_2 vector.

When integrating Eq. (A1) in the Doppler limit, where $\gamma_{mn}, \kappa v_T \ll \omega_D$, one can tend $\text{Im}(v_{xj})$ and $\text{Im}(v_{zj})$ to zero and use the symbolic equation valid for $\alpha \rightarrow 0$

$$\frac{1}{x - a - i\alpha} = i\pi \text{sgn}(\alpha) \delta(x - a) + P \frac{1}{x - a}, \quad (\text{A6})$$

where P means the principal value of the integral. The right-hand side of Eq. (A1) contains the factor $(v_{z1} - v_{z2})^{-1} = \{(\Delta_1 + i\gamma_{eg})/k_1 - [\Delta_3 + i(\gamma_{e'g} - \gamma_{g'g})]/k_3\}^{-1}$ which is essentially nonzero in the vicinity of the resonance

$$\frac{\Delta_1}{k_1} = \frac{\Delta_3}{k_3}. \quad (\text{A7})$$

Under such a condition the principal values of the integrals over v_z appearing in integrating Eq. (A1) cancel each other. We assume for definiteness that $k_1 > 0$ and $\gamma_{e'g} > \gamma_{g'g}$. Then the molecules arriving at the surface give a nonzero resonant contribution determined by the δ functions if $k_3 < 0$. To ensure the resonance condition for such molecules it is necessary to have $\Delta_1 < 0$ and, as it follows from Eq. (A7), also $\Delta_3 > 0$. The remaining averaging over v_y does not change the result and we come to Eq. (50) given in the text.

The contribution from desorbed molecules can be written in the form of Eq. (26) with the following substitutions:

$$A(\mathbf{v}) \rightarrow A(\mathbf{v}'), \quad (\text{A8})$$

$$B(\mathbf{v}) \rightarrow B(\mathbf{v}'; \kappa \rightarrow -p_z, k_1 \rightarrow -k_3), \quad (\text{A9})$$

$$C(\mathbf{v}) \rightarrow C(\mathbf{v}'; \kappa \rightarrow -p_z, k_1 \rightarrow -k_3). \quad (\text{A10})$$

Its averaging over velocities can be carried out much as it has been done for arriving molecules and we obtain as a result Eq. (51).

APPENDIX B: CONTRIBUTION OF DIRECTLY SCATTERED MOLECULES

We shall consider here the contribution of the first term in the square brackets in Eq. (29). The assumption that the scattering kernel has the form (53) allows one to remove the integration over \mathbf{v}'_{\parallel} and to take all the functions at $\mathbf{v}'_{\parallel} = \mathbf{v}_{\parallel}$. The corresponding integrand contains the factor which can be represented as follows:

$$\frac{A(\mathbf{v})B(\mathbf{v})}{v_z'^2 [ik_{sz} - p_2(\mathbf{v}')] [ik_{sz} - p_3(\mathbf{v}')] } = - \frac{1}{k_1 k_2^3 (v_z - v_{z1}) [v_x - v_{x1}(v_z)] [v_x - v_{x3}(v_z')] [v_x - v_{x4}(v_z')] }, \quad (\text{B1})$$

where

$$v_{x3}(v_z') = \frac{1}{k_2} [-\Delta_1 + \Delta_2 - (k_3 - k_{sz})v_z' - i\gamma_{g'g}], \quad (\text{B2})$$

$$v_{x4}(v_z') = \frac{1}{k_2} (-\Delta_m + k_{sz}v_z' - i\gamma_{e'g}), \quad (\text{B3})$$

and the quantities v_{z1} and $v_{x1}(v_z)$ are given by Eqs. (A4) and (A2), respectively.

The product on the right-hand side of Eq. (B1) can be decomposed into a sum of three elementary fractions $(v_x - v_{xj})^{-1}$ each of which can be in turn decomposed into elementary fractions $(v_z - v_{zj})^{-1}$ and $(v_z' - v_{zj}')^{-1}$. As a result, each term will be proportional to the factor $[\Delta_1 + \Delta_3 + i(\gamma_{eg} + \gamma_{e'g} - \gamma_{g'g})]^{-1}$ which is essentially nonzero in the vicinity of the resonance

$$\Delta_3 = -\Delta_1. \quad (\text{B4})$$

We shall assume for simplicity that the quantities κ and k_{sz} can be neglected in comparison with k_v . Then in the Doppler limit one can use Eq. (A6) when integrating Eq. (B1) over velocities. Taking also into account the condition (B4) and assuming that the scattering kernel varies slowly at a scale of γ_{mn}/k_v , we come to Eq. (55) given in the text.

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