

Collision-induced Spectra at a Gas-Solid Interface

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Abstract

In analogy with collision-induced translational absorption in the far infrared in binary mixtures of inert gases, it is suggested that a similar process must occur at a gas-solid interface. Each gas molecule develops a dipole moment that depends on its distance from the surface, and its time dependence due to the thermal motion of the molecule should cause optical activity. The necessary theory and expected absorption curves for a typical model are given.

Collision-induced far infrared absorption in binary mixtures of inert gases has been studied extensively, both experimentally and theoretically (Kiss and Welsh 1959; Bosomworth and Gush 1963; Poll and van Kranendonk 1961; Tanimoto 1965; Okado *et al.* 1968; Birnbaum and Cohen 1976; Shlyapnikov and Shmatov 1980). The reason for this optical activity is the net induced dipole moment in an unlike pair of atoms, which fluctuates due to their random motion. In the proximity of a solid surface an atom develops a dipole moment, and the functional dependence of this induced moment on the atom-surface distance is known, at least in the asymptotic region (Antoniewicz 1974). Because of the thermal motion of the gas atoms colliding with the surface, the induced moments on them become time dependent and should cause optical activity.

A simple theory for the absorption spectrum line shape can be developed as follows. From the Kubo formula (Kubo 1959; Birnbaum and Cohen 1976) the absorption coefficient of the gas with N molecules in volume Ω is given by

$$B(\omega) = \frac{4\pi^2}{3\hbar c} \omega \left\{ 1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right) \right\} N J(\omega), \quad (1)$$

where

$$J(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\omega t) \langle \mu(0) \mu(t) \rangle dt, \quad (2)$$

with μ the induced moment on the gas atom. It is presumed here that the number density $n = N/\Omega$ of the molecules is a constant throughout the container, despite the weak interaction between a gas atom and the solid.

If the experimental set-up involves the radiation travelling parallel to a planar solid surface, the thermal average need be taken only with the component of the motion normal to the surface, the induced moment being always in that direction. This can be done classically, corresponding to the one-dimensional Hamiltonian of a gas atom

$$H_0 = \frac{1}{2}mv^2 + V(z), \quad (3)$$

where the z -axis is normal to the surface at $z = 0$, v is the velocity of the atom along the z -axis, and $V(z)$ is the interaction potential between the atom and the surface. Then, noting that the induced moment exists only for $z \geq 0$, we get

$$\begin{aligned} N\langle\mu(0)\mu(t)\rangle &= n\Omega\left\{\int_{\Omega} d^3r \exp\left(-\frac{V(z)}{k_B T}\right)\mu(z)\right. \\ &\times \left.\int_{-\infty}^{\infty} \mu(|z-vt|) \exp\left(-\frac{mv^2}{2k_B T}\right) dv\right\} / \left\{\int_{\Omega} d^3r \exp\left(-\frac{V(z)}{k_B T}\right) \int_{-\infty}^{\infty} dv \exp\left(-\frac{mv^2}{2k_B T}\right)\right\} \\ &= nS\left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \frac{1}{Q(T)} \frac{1}{|t|} \int_0^{\infty} dz \int_0^{\infty} du \mu(z)\mu(u) \exp\left(-\frac{V(z)}{k_B T}\right) \\ &\times \left\{\exp\left(-\frac{m(u+z)^2}{2k_B T t^2}\right) + \exp\left(-\frac{m(u-z)^2}{2k_B T t^2}\right)\right\}, \end{aligned} \quad (4)$$

with

$$Q = \frac{1}{L} \int_0^L dz \exp\left(-\frac{V(z)}{k_B T}\right). \quad (5)$$

Here L is the length of the container in the z -direction, and in (4) the limit $L \rightarrow \infty$ is implied, while S is the surface area, so that $\Omega = SL$.

Equations (4), (2) and (1) give the theory, in which the inputs are the atom-surface potential $V(z)$ and the induced moment $\mu(z)$. The main contribution in (4) comes from small z where $\mu(z)$ is large. The form of $\mu(z)$ for small z is not known accurately, although an exponential dependence may be expected due to exchange effects. To get a qualitative look at the expected absorption curves, we ignore $V(z)$ and assume that

$$\mu(z) = \mu_0 \exp(-\lambda^2 z^2). \quad (6)$$

Then, we get

$$N J(\omega) = \frac{\mu_0^2 n S}{2\lambda^2} \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} K_0\left\{\omega\left(\frac{m}{\lambda^2 k_B T}\right)^{\frac{1}{2}}\right\}, \quad (7)$$

$$B(\omega) = B_0 n S \frac{\omega}{\omega_1} \left(\frac{\hbar\omega_1}{k_B T}\right)^{\frac{1}{2}} \left\{1 - \exp\left(-\frac{\omega}{\omega_1} \frac{\hbar\omega_1}{k_B T}\right)\right\} K_0\left\{\frac{\omega}{\omega_1} \left(\frac{\hbar\omega_1}{k_B T}\right)^{\frac{1}{2}}\right\}, \quad (8)$$

where $B_0 = (2\pi^3)^{\frac{1}{2}} \mu_0^2 / 3\hbar\lambda c$, and $\omega_1 = \hbar\lambda^2/m$ is a natural unit of frequency for the system. Further, K_0 is the modified Bessel function of order zero.

The parameter λ is expected to be of the order of \AA^{-1} ($1 \text{\AA} \equiv 10^{-10} \text{ m}$) for an atom-metal system, so that $\hbar\omega_1 \sim (m_e/m) \times (\text{Rydberg constant}) \sim 10^{-3} \text{ eV}$ for a helium atom, corresponding to a temperature of $T_c \sim 11 \text{ K}$ or the wave number

$\sim 8 \text{ cm}^{-1}$. Fig. 1 gives a plot of the absorption curves at various ambient temperatures for such a system. The absorption region is the same as that in binary mixtures of inert gases.

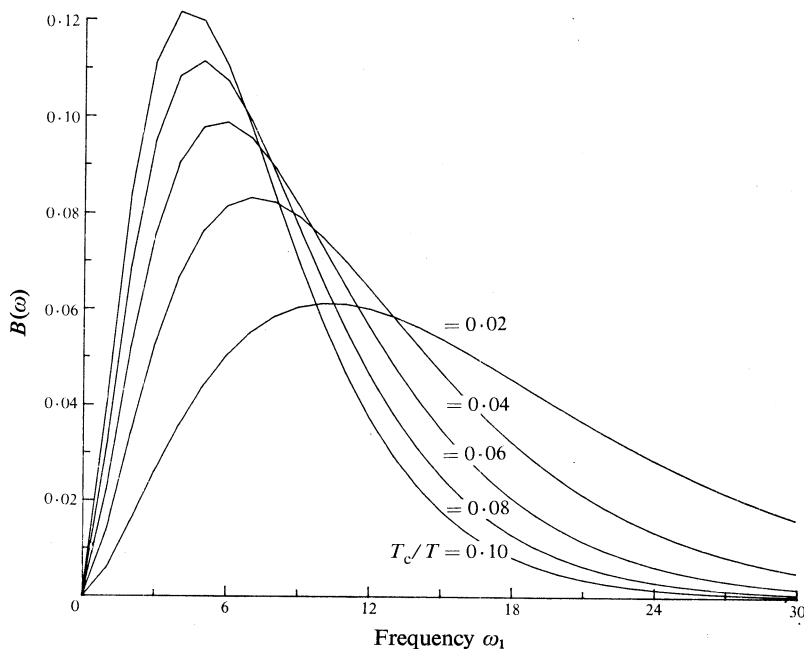


Fig. 1. Absorption curves at the various ambient temperatures indicated for an atom-metal system. The frequency is in units of ω_1 , and $B(\omega)$ in units of $(B_0 n)S$.

The experiments of Bosomworth and Gush (1963) on inert gas mixtures were performed at a total pressure of about 100 atm ($\equiv 1.01 \times 10^3$ kPa) and an absorption pathlength of 3 m. The more recent experiments of Bar-Ziv and Weiss (1976) used the same pressure range and a path length of 2 m. Since B_0 of equation (8) is of the same order as that arising between the inert gas pair, the translational absorption at a gas-solid interface should be observable in similar experimental conditions.

It has been pointed out that the translational spectrum of a binary mixture is useful for determining both the inter-atomic potential and the induced moment as a function of the separation distance of an unlike pair of atoms (Futrelle 1967; Shlyapnikov and Shmatov 1980). Obviously, the same feature exists in the interface absorption spectrum for determination of $\mu(z)$ and $V(z)$.

References

- Antoniewicz, P. R. (1974). *Phys. Rev. Lett.* **32**, 1424.
- Bar-Ziv, E., and Weiss, S. (1976). *J. Chem. Phys.* **64**, 2412.
- Birnbaum, G., and Cohen, E. R. (1976). *Can. J. Phys.* **54**, 593.
- Bosomworth, D. R., and Gush, H. P. (1963). *Can. J. Phys.* **43**, 729; 751.
- Futrelle, R. P. (1967). *Phys. Rev. Lett.* **19**, 479.
- Kiss, Z. J., and Welsh, H. L. (1959). *Phys. Rev. Lett.* **2**, 166.
- Kubo, R. (1959). In 'Lectures in Theoretical Physics', Vol. 1 (Eds W. E. Britten and L. G. Dunham), p. 151 (Interscience: New York).

- Okado, K., Kajikawa, T., and Yamamoto, T. (1968). *Prog. Theor. Phys. Jpn* **39**, 863.
Poll, J. D., and van Kranendonk, J. (1961). *Can. J. Phys.* **39**, 189.
Shlyapnikov, G. V., and Shmatov, I. P. (1980). *Sov. Phys. JETP* **52**, 1050.
Tanimoto, O. (1965). *Prog. Theor. Phys. Jpn* **33**, 585.

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