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COMMENTS

Comment on "Resonance Raman Scattering and Collision-Induced Redistribution Scattering in I_2"

P. A. Hackett

Division of Chemistry, National Research Council of Canada, Ottawa, K1A OR6, Canada

The form of resonant scattering spectra and their time decays are restated. An analysis of recent experimental results on molecular iodine shows that the existence of elastic collisional transfer processes cannot be positively proved.

In a recent Letter Rousseau, Patterson, and Williams (RPW) claim to present the "first experimental observation" of collisionally induced redistribution scattering.[1] This has been defined for resonance scattering of monochromatic light in gases[2] as the process by which *elastic* collisions between atoms redistribute the scattered radiation from the excitation frequency (ν_0) over the absorption profile of the atomic resonance centered at $\nu_0 - \Delta\nu$. The effect of collisions on the form of resonance scattering spectra has long been recognized. In an early review[3] of the subject it was noted that in the limit of Doppler-broadened absorption lines the scattered light observed in a direction parallel to the direction of the exciting radiation has a spectral distribution which is closely related to that of the exciting radiation, e.g., if the exciting radiation is self-reversed, the emission line is also self-reversed.[4] However, when the absorption linewidth is dom-

inated by collisional perturbations the emission line has exactly the same shape as the absorption line, whatever the excitation frequency or profile, and independent of the angle of viewing.[5] It was concluded that "the Rayleigh scattering persists only in those parts of the spectrum where the absorption caused by Doppler broadening or collision broadening of the absorption line practically vanishes."[3] These observations, together with the effect of *elastic* collisions, were fully included in the theory developed by Hüber to explain line shapes observed during resonant scattering of monochromatic light in gases.[2] There have been no experiments which demonstrate the elastic redistribution effect. Such an effect, and its dependence on $\Delta\nu$, may be of prime importance in theories describing the Raman effect.

It is the purpose of this paper to point out that the experiments performed by RPW[1] do not provide evidence for elastic collisional redistribu-

tion. In particular two factors which can account for the results observed by RPW are stressed. These factors are the finite linewidth of the excitation source and the occurrence of inelastic collisions; a method of numerically estimating the importance of these two effects is then outlined.

Resonance scattering in the absence of collisions.—The scattered light from a molecular resonance excited by a source of finite spectral width decays with two characteristic decay times, that of the excitation source and that of the excited state.[6] Fourier transform analysis[7] of the time-decay formulas or simple consideration of the requirement of strict energy conservation between the absorbed and emitted photon requires that the line shape of the scattered light [$S(\nu)$] be given by

$$S(\nu) = A(\nu) I(\nu), \tag{1}$$

where $A(\nu)$ describes the probability that a photon of frequency ν will be absorbed, and $I(\nu)$ describes the intensity profile of the excitation source. When $\Delta\nu$ is large $S(\nu)$ can be approximated by a doublet, with one component centered at ν_0 with the linewidth ($\Delta\nu_s$) and decay time of the excitation source, the other centered at $\nu_0 - \Delta\nu$ with the linewidth ($\Delta\nu_r$) and decay time characteristic of the resonance. However RPW interpret their results[1] using a formula developed by Hüber[2] to describe the resonant scattering of *monochromatic* light. In this approximation only the component centered at ν_0 is present. The light source used by RPW is pulsed[8]; hence the uncertainty principle constrains that it have a finite spectral width greater than or equal to the linewidth of the inverse Fourier transform of the time profile of the pulse.[9] Hence one would expect to observe long-lived emission centered at $\nu_0 - \Delta\nu$ (the lines labeled S', O', and P'[1]) even in the absence of collisions.

Effect of collisions on light-scattering spectra. —The effect of elastic collisions cannot be considered without considering the effect of other collisional processes, as all these effects have the same pressure dependence. The gross effects of pressure on the system studied by RPW can be summarized as follows: As the pressure of the scattering gas increases (i) the magnitude of $A(\nu)$ increases in a nonlinear manner, according to the Beer-Lambert law; (ii) the rate of inelastic collisional processes (collisional transfer,[10] self-quenching[11]) increases with resultant decrease in quantum yield of resonantly scattered

light, decrease in emission lifetime (τ_D), and change in shape of $A(\nu)$[12] and hence in $S(\nu)$; (iii) the rate of collisional transfer increases with resultant increase in intensity of nonresonantly scattered light[10,13]; (iv) the rate of elastic collisional redistribution increases, transferring intensity from the component centered at ν_0 to that centered at $(\nu_0 - \Delta\nu)$.[2] RPW consider only process (iv) in the absence of all other effects. I will proceed to examine their data in light of all four collisional effects and the effect of finite excitation linewidth.

Data presented by RPW.—RPW present two emission-decay curves measured in the first Stokes band of molecular iodine excited by the argon laser line at 5154 Å.[1] They assert that the long-lived contribution is greatly increased at 0.25 Torr over that measured at 0.03 Torr. I have inspected the two decay curves and conclude that the integrated intensity of the long-lived contribution only increased by 15%; moreover the integrated intensity of the short-lived emission is approximately equal to that of the long lived at both pressures. I also note that the decay time of the long-lived component is considerably greater at 0.03 Torr than at 0.25 Torr.

I suggest that these data are clear qualitative evidence for the importance of the effects discussed in the preceding two sections. Thus the long-lived component observed at 0.03 Torr is due to the finite laser linewidth, and the decrease in the lifetime of the long-lived component at 0.25 Torr is clear evidence for inelastic collisional processes, since elastic processes do not change the quantum state.

RPW present a high-resolution spectrum of part of the emission spectrum excited at 0.25 Torr. The spectrum consists of coherently scattered lines, labeled S, Q, and O and lines labeled S', Q', and O' which the authors claim to be due principally to redistribution scattering. However, a previously published spectrum[10] of the entire first Stokes band of molecular iodine excited by the 5145-Å Ar line at the lower pressure of 0.03 Torr shows strong evidence for collisions which transfer rotational and/or vibrational energy. The 5145-Å line is in resonance with the $P(n)$ and $R(n+2)$ lines of the $43 \leftarrow 0$ vibrational band of the $B\,^3\Pi_{0_u^+} \leftarrow X\,^1\Sigma_{0_g^+}$ transition ($n = 12$,[10] $n = 13$[1]). Such transitions produce states with rotational quantum numbers equal to $(n-1)$ and $(n+3)$. It is well known that collisional transfer in iodine can produce only even changes in rotational quantum number,[13] since alternate rota-

TABLE I. Results of numerical estimates.

Pressure (Torr)	P_R	P_C	$\Delta\nu_r$ (cm^{-1})	τ_D (μsec)
0.03	0.390	0.041	0.016	1.2
0.25	0.072	0.014	0.020	0.30

TABLE II. Results of intensity calculations. O. D. is the optical density at ν_0 and 0.03 Torr. LP and FP stand for Lorentzian pulse and Fourier pulse, respectively.

O.D.	I_{RR}/I_{RF} at 0.03 Torr LP	FP	I_{RR}/I_{RF} at 0.25 Torr LP	FP
0.0003	0.50	8.87	5.01	0.72
0.003	0.50	8.87	5.01	0.74
0.03	0.50	8.87	5.02	0.83
0.3	0.59	8.92	5.09	1.63
3.0	1.61	9.30	5.08	4.18

tional states have opposite symmetry. Hence inelastic collisions are able to transform the lines labeled S, Q, and O, either by a single collision $[(n-1) \rightarrow (n+3)]$ or by multiple collision route $[e.g., (n-1) \rightarrow (n-5) \rightarrow (n-1)]$.

Numerical estimates.—In order to qualitatively assess the importance of the effects discussed above I have performed model calculations of the system investigated by RPW.[1]

The known values of the radiative rate constant (k_R) of $I_2[B\ ^3\Pi_{0_u^+}(\nu'=43)]$,[13] the self-quenching rate constant (k_{SQ}) for this state,[13] and the rate constants for collisional transfer within this state to specific rovibronic final states[11] were employed to calculate the pressure-dependent probability (P_R) that a molecule will radiate before suffering a collision:

$$P_R = k_R / \{k_R + [I_2](k_{SQ} + \Sigma k_T)\}, \qquad (2)$$

where $[I_2]$ is the iodine pressure.

The time-averaged, pressure-dependent probability that a molecule will radiate from the monitored levels after suffering a collision (P_C), was calculated by computer integration of the population of the monitored levels over several emission decay times. This integration was performed using a matrix of 51 collisional transfer cross sections[10] and 85 rovibronic levels.

Molecules radiating without suffering a collision do so with a line shape given by Eq. (1). $A(\nu)$ was calculated using readily available formulas[12] for the Doppler linewidth, the natural linewidth, and the total effective linewidth for collisional transfer and self-quenching at 0.03 and 0.25 Torr. $I(\nu)$ was approximated in two ways: by a smooth curve passing through the maxima of the inverse Fourier transform of the time profile of the laser pulse[1,9] (Fourier pulse) and by a Lorentzian frequency profile of 20-MHz linewidth[14] (Lorentzian pulse). The integrated intensity of light scattered with the linewidth of the laser (I_{RR}) is then approximated by

$$I_{RR} = P_R \frac{S(\nu_0)\Delta\nu_s}{S(\nu_0)\Delta\nu_s + S(\nu_0 - 1.7\ \text{GHz})\Delta\nu_r},$$

while the integrated intensity of light scattered with the linewidth of the absorption line (I_{RF}) is approximated by

$$I_{RF} = P_R - I_{RR} + P_C.$$

The results of these numerical estimates are summarized in Tables I and II. These results were not significantly altered by including a 12-Å cross section for elastic transfer in the matrix of transfer rates used in the calculation.

The results presented in Table II indicate that the ratio of integrated intensity of long-lived emission is sensitive to many experimental parameters, e.g., line shape of excitation source, optical density, and pressure. Other parameters may also affect the measured intensities, e.g., scattered light, and impurities. It would therefore seem unreasonable to use two measurements to prove the occurrence of elastic collisional transfer in this complex system.

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Transient Effects in Low-Temperature Specific Heat of Amorphous Dielectrics

J. Heinrichs and N. Kumar*

Institut de Physique, Université de Liège, Sart-Tilman, Belgium

(Received 7 July 1975; revised manuscript received 24 March 1976)

We show that recent short-time-scale measurements of the specific heat of amorphous dielectrics are not inconsistent with the predictions of the tunneling model if the associated heat diffusion problem is properly treated. This requires taking into account the kinetics of energy transfer between the phonons and the tunneling modes.

In a recent Letter Goubau and Tait[1] presented short-time-scale ($t \sim 100$ μsec) measurements of the specific heat of some amorphous dielectrics, which agree with the earlier long-time results[2,3] within the experimental uncertainty. They concluded that these results contradict the tunneling model[4,5] in that the latter would require the long-time specific heat to exceed the short-time value[1] by a factor of 3 to 4. The tunneling model assumes the existence of localized two-level structural states in amorphous dielectrics and was introduced previously to interpret the thermal properties of these systems.[4,5]

The purpose of the present Comment is twofold. First we show that the above measurements are indeed consistent with the tunneling model provided that the heat diffusion problem is treated correctly, taking into account the kinetics of the energy transfer between the phonons which carry the heat and the localized two-level tunneling systems. Secondly, for an ideal situation of uniform spatial heating of the sample, we derive explicitly the intrinsic time dependence of the specific heat in the dominant-phonon approximation and discuss some limiting cases. By "intrinsic" we refer to the time dependence arising entirely from the delayed transfer of energy[4-6] from the phonons to the two-level systems in the absence of heat diffusion.

We consider the experimental situation where a slab of unit cross-sectional area confined to the region $0^- < x < L$ is heated by a heat pulse at $x = 0$, at $t = 0$. The temperature gradient $\partial T(x,t)/\partial x$ is maintained zero[1] at $x = 0^-$ and $x = L$ for all

$t > 0$. The heat transport is governed by

$$\partial Q(x,t)/\partial t = \kappa \partial^2 \Delta T(x,t)/\partial x^2, \qquad (1)$$

where $\partial Q(x,t)/\partial t$ is the rate of accumulation of heat per unit volume and κ is the thermal conductivity. This heat is taken up instantaneously by the phonons which then slowly transfer part of it to the local tunneling states. We describe the kinetics of this heat transfer in the dominant-phonon approximation in which the thermal phonons are replaced by an effective number, N_p, of phonon modes per unit volume, having energy $E_p \equiv E = 3k_B T$. The latter are assumed to interact only with an effective number N_t of pairs of resonant tunneling states per unit volume, of energy splitting $E_t \equiv E$. We denote by $n_p(x,t)$ the phonon occupation number density per mode and assume that the phonon subsystem is always locally in thermal equilibrium. Thus the local (phonon) temperature is defined and a change $\Delta n_p(x,t)$ corresponds to a change ΔT in the measurable temperature given by ($\beta = 1/k_B T$)

$$\Delta n_p = \frac{\beta E}{4T \sinh^2(\frac{1}{2}\beta E)} \Delta T \equiv a \Delta T. \qquad (2)$$

The time evolution of $n_p(x,t)$ is determined by

$$\frac{\partial n_p}{\partial t} = \frac{a}{\rho c_p(T)} \frac{\partial Q(x,t)}{\partial t} + \left(\frac{\partial n_p}{\partial t}\right)_t, \qquad (3)$$

where the first term gives the change in the phonon occupation due to the inflow of heat $\partial Q(x,t)/\partial t$ into an element of thickness Δx and $(\partial n_p/\partial t)_t$ represents the rate of change of the phonon occupation due to resonant interaction with the lo-