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

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

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We demonstrate that neither laser broadening nor inelastic collisional broadening plays a dominant role in the data of our recent experiments as has been suggested, and again we conclude that our results can only be explained by redistribution emission resulting from phase-changing processes.

In a recent Letter[1] we reported temporal and frequency measurements on the re-emitted light following slightly off-resonance monochromatic excitation of molecular iodine. We interpreted our data as clear evidence for collisional redistribution—an effect predicted some years ago[2] but not previously observed. This process is one in which a molecule undergoes a collision resulting in a change of phase but it remains in the same quantum state, i.e., it is a pseudoelastic collision. Similar observations were subsequently made in atomic sodium by Carlsten and Szöke.[3]

Recently, however, Hackett[4] claimed that our interpretation was incorrect on account of two effects of different origin that would result in qualitatively similar data. These are exact resonance excitation due to the unavoidable lack of precise monochromaticity in the incident laser pulse, and exact resonance excitation due to inelastic collisional processes in which a state from which we see emission has been populated by a transfer process from another state initially prepared by the laser.

Both the lack of perfect monochromaticity and the occurrence of inelastic collisions are effects that we recognized could potentially contribute to light re-emission at the resonance frequency and could therefore be misinterpreted as redistribution re-emission. Indeed, both of these effects were considered by us prior to our original publication[1] and then, as now, they can be readily eliminated from consideration as playing an important role in the re-emission properties for the case of molecular iodine under the conditions of our experiments.

The unimportance of these effects in our experimental results may be seen readily by inspection of published data. First from the lifetime data (Fig. 2 of our previous Letter[1] and Fig. 1 in this Comment) there is a clear difference in the pressure dependence of the two processes as may be seen by observing the intensities of the two re-emission components at the termination of the laser pulse. As the pressure is increased, the ratio of the long-lived process to the short-lived process increases roughly linearly with pressure. This is due to the fact that the intensity due to the collisional processes increases quadratically with pressure while that due to the Raman process increases linearly with pressure. This result rules out Hackett's proposal of laser broadening as the explanation of our data since the corresponding intensity would, just as for the Raman scattering, increase linearly with pressure, and the ratio would be the same at both pressures. The data then require that a collisional process be responsible for the effects we observe. A measure of the importance of the inelastic collisional processes referred to by Hackett[4] to the total collisional re-emission may be obtained by examination of the spectral distribution of the emission following excitation at 5145 Å (Fig. 1 in Kurzel *et al.*[5] and Fig. 2 in this Comment). Here only the expected S, Q, and O branch triplet is strong. The weak transfer bands seen on either side of the triplet serve as a calibration of the effect of inelastic collisional processes; and their weakness gives a qualitative indication that such processes are not important. From this cursory inspection of the temporal and spectral data, it is apparent that laser broadening and inelastic collisions are not important and that only pseudo-elastic collisions can account for the phenomena that we have observed. In the remainder of this Comment we present a quantitative examination of these data which support these qualitative con-

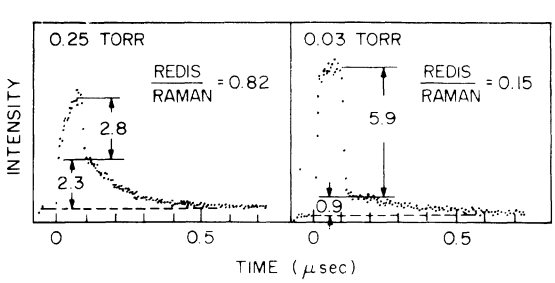

FIG. 1. Experimental time decay of the Raman and redistribution re-emission at two pressures. The integration time for each decay curve is different. As the pressure is increased the ratio of the redistribution to the Raman intensity increases roughly linearly with pressure.

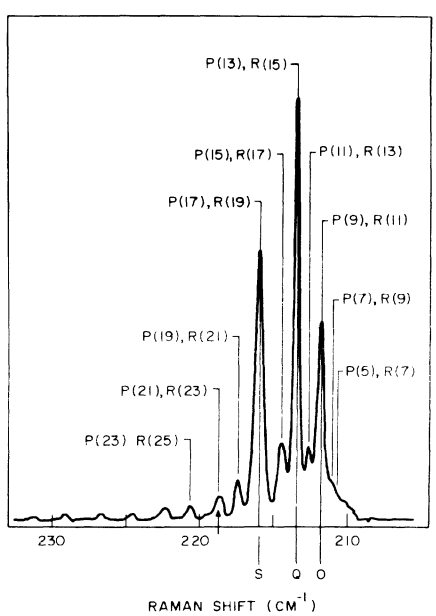

FIG. 2. Raman scattering spectrum of the S, Q, and O triplet at 213 cm^{-1}. The labeling gives the assignment of the origin of each line (see text). The weak lines (all but the triplet) result from inelastic collisional transfer processes. The line indicated by the arrow at about 218 cm^{-1} can be used to calibrate the importance of $\Delta J = 4$ transfer processes.

clusions.

It is well known and has been pointed out by several authors[6] that when an incident light field of finite width[7] is nearly resonant with a sharp transition one can in principle see two re-emission frequencies. One is centered at the frequency of the incident light and may appropriately be termed a Raman process; and the other is centered at the frequency of the transition under consideration. This latter re-emission results from the tail of the light field that extends through the center of the absorption band. This tail may result from the finite width of the light field in a cw experiment or may result from the unavoidable frequency broadening in a pulsed experiment due to turning the field on or off rapidly. The relative intensity of the two re-emission frequencies depends on the specific line-shape functions that characterize both the resonant transition and the incident light field.

A measure of the importance of this contribution to the re-emission data which we reported[1,8] may be readily obtained by a detailed consideration of the pressure dependence of the temporal response.[1,8] Raman scattering increases linearly with pressure because of the linear increase in the I_2 molecular density. In contrast, a collisional process increases quadratically with pressure. The intensity due to resonant excitation from frequency broadening, as suggested by Hackett, should also increase linearly with I_2 pressure just as the off-resonance Raman scattering does.

The relative pressure dependence of the two types of re-emission that we observe may be seen from the lifetime data[1,8] by using the Raman scattering (instantaneous process) as a standard. This relative intensity can be measured by comparing the intensity of the instantaneous process to the long-lived process at termination of the laser pulse for the two pressures. Relative intensity measurements are necessary since, because of fluctuations in laser power, different integration times, and possible alignment differences, a direct comparison of intensities without an internal standard from one experiment to another cannot be made. As the pressure is increased from 0.03 to 0.25 Torr the I_2 density increases by a factor of 8.3. The experimental ratio of the long-lived to instantaneous intensity *increases by a factor of 5.5* (see Fig. 1). After making a minor quenching correction at the higher pressure, on the basis of our redistribution model *we predict an increase of a factor of 6.6* In contrast, *Hackett's model of laser broadening predicts a decrease by a factor of 0.8.* This intensity decrease results from the above-mentioned quenching effect without which the long-lived to short-lived ratio would be insensitive to pressure under the assumption of laser broadening. Within experimental error our calculations clearly demonstrate that a collisional process is occurring at the higher I_2 pressure.

Hackett[4] also asserted that our long-lived re-emission may have resulted from inelastic effects. He argued that the two states prepared by our 5145-Å excitation may be transformed one to the other by inelastic collisional processes. An accurate estimate of the magnitude of this process may be obtained readily by a detailed examination of the fluorescence data.

In the region of 5145 Å used in our experiments, two excited electronic state levels may be prepared simultaneously.[9] They are $v' = 43$, $J = 12$, and $v' = 43$, $J = 16$. Because of the $\Delta J = \pm 1$ selection rule in a radiative transition, emission from each of these levels results in a doublet; and since one is a P and one is an R transition, their overlap gives a triplet in the Raman spectrum[5] which we show in Fig. 2. This is a 0.5-cm^{-1} resolution spectrum of the Raman-shifted re-emission from I_2 in the 213-cm^{-1} region obtained with 5145-Å resonant excitation from a room-temperature sample (I_2 pressure ~0.25 Torr). Similar relative intensities of the structure were observed when the laser was shifted out of resonance with the transitions. The origin of each line is indicated on the top using the assignments given by Kurzel *et al.*[5] except the values of the rotational quanta have been increased by one to be consistent with the more recent assignment[9] of the 5145-Å excitation resulting in $P(13), R(15)$ transitions rather than $P(12), R(14)$ transitions. In considering only the ground electronic state levels, the triplet may be treated as S, Q, and O branch Raman transitions—the S branch originating from the $P(17)$ transition, the Q branch from the $P(13)$, $R(15)$ transitions, and the O branch from the $R(11)$ transition. All the other features result from inelastic collisional transfer processes.

The selection rule for transfer of rotational energy through collisions is $\Delta J = \pm 2n$. Consequently, as indicated by Hackett,[4] $\Delta J = 4$ collisions between the $J = 12$ and $J = 16$ levels of the excited state will give a result experimentally indistinguishable from the redistribution type of process. We consider only the $\Delta J = 4$ type of collision because the multiple collision route suggested by Hackett[4] can be shown to be negligible ($\approx 1\%$) by inspection. A

semiquantitative estimate of the magnitude of $\Delta J = 4$ collisional processes interchanging $J = 12$ and $J = 16$ may be made by examining the $\Delta J = 4$ processes $J = 12 \rightarrow J = 8$ and $J = 16 \rightarrow J = 20$. Re-emission from the $J = 8$ and $J = 20$ levels has frequencies experimentally separable from $J = 12$ and $J = 16$ re-emission allowing identification of these transitions.

Re-emission from $J = 8$ and $J = 20$ gives the $P(9)$, $R(7)$ and the $P(21), R(19)$ transitions, respectively, in Fig. 2. $P(9)$ and $R(19)$ coincide with the O and S branches, respectively, so may not be used as a $\Delta J = 4$ calibrant; and the $R(7)$ is not well resolved. The $P(21)$ line, however, is separated and well resolved (see arrow on abscissa in Fig. 2) and occurs in coincidence with an $R(23)$ line obtainable by $\Delta J = 8$ from the $J = 16$ level. Note also that a $P(21)$ line may also result from a $\Delta J = 8$ transition from the $J = 12$ level. Rough estimates of the importance of $\Delta J = 8$ transitions may be obtained by examining the intensity of other transfer lines further away, and thereby enable us to place an upper limit on the contribution of the $\Delta J = 4$ collisional process to the intensity of the $P(21), R(23)$ line indicated by the arrow in Fig. 2. This intensity ($\frac{2}{3}$ of the total intensity of this line) may then be used to set an upper limit on the contribution of inelastic collisions to the S branch.

Emission at the S branch frequency may result from radiative emission from the $J = 16$ level, $P(17)$, populated by the incident photon field (the primary process), emission from $J = 16$, $P(17)$, populated by the $\Delta J = 4$ collision from $J = 12$, and emission from the $J = 20$ level, $R(19)$, populated by the $J = 16 \rightarrow J = 20$, $\Delta J = 4$ collisional process. Using $P(21)$ as a calibration *an upper limit of 10% may be placed on the $\Delta J = 4$ transfer process contribution to the intensity of the S branch.* Therefore in our previously published temporal and spectral data[1,8] we may place an upper limit of 20–25% on the contribution from inelastic collisional transfer processes to the broadened or long-lived re-emission that we observed.

Finally, Hackett[4] argued that our conclusions are suspect because our results are sensitive to uncertainties in the parameters which we have discussed here. However, we have shown that both laser broadening and inelastic collisions may be ruled out as dominant contributors to the long-lived re-emission that we reported.[1,8] In addition, a thorough theoretical analysis of our data was made recently by Mukamel, Ben-Reuven, and Jortner[10] in which parameters appropriate for I_2 were used to obtain numerical simulations of the time-resolved data. In that study[10] a quantitative confirmation of our qualitative conclusions were made. On the basis of that work[10] and on the basis of the analysis presented here of the criticisms raised by Hackett, we reassert our original conclusions[1,8] that in our off-resonance excitation experiments, the long-lived frequency-shifted and broadened re-emission results primarily from pseudoelastic phase-changing collisions.

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