Origin of Resonant Raman Excitation Profiles Red-Shifted from Optical Absorption Profiles

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We observe that the Raman excitation profile in matrix-isolated Br_2 is significantly red-shifted from the absorption maximum and show that a straightforward relationship between the two can in general not be expected. A simple theory considering only the resonant contributions describes our data reasonably well. In addition, we discuss the effect on our results of interference between the B and ${}^1\Pi_{1u}$ states.

Considerable attention is currently being given to the determination of the basic mechanism of resonance Raman scattering.[1,2] Concurrently it is being used as a tool for interpreting complex absorption spectra. Typically[3] comparisons are made between the absorption spectrum and the spectrum of the intensity of a given Raman mode versus the excitation frequency used to excite the scattering (excitation profile); and in some cases the agreement between the two spectra is good.[3,4] On the other hand, such a comparison made in some complex systems[5-7] reveals that the peak of the excitation profile is red-shifted from the absorption maximum, a result that does not fit readily into the existing theoretical framework. These include studies of I_2 charge-transfer complexes[5,6] and tetrocyanoethylene charge-transfer complexes.[7] While in neither case could a quantitative explanation be offered, proposals were made that the effect resulted from either interference between nearby and higher-lying states[6] or frequency-dependent damping factors[7] resulting in a reduction in lifetime of the higher-energy vibronic states. A study of a simple system whose spectroscopy is well understood is therefore desirable.

In the present work we have studied the excitation profile of Br_2 isolated in an argon matrix at 5–10°K, whose potential functions, energy levels, and spectroscopic term values are quite well known. Both the B (${}^3\Pi_{0^+u}$) and the X (${}^1\Sigma_{0^+u}$) state potential functions are known to be negligibly perturbed by the solid medium, except for a ~480-cm^{-1} differential shift to lower energies.[8] We observe that the excitation profile of the Raman fundamental at ~315 cm^{-1} is red-shifted significantly from the absorption maximum; and we present a simple model, based on the consideration of Franck-Condon factors and density of states, which is consistent with our data. In addition, we discuss interference effects which also influence the excitation profile. We conclude that in general the peak of the excitation profile need not coincide with the absorption maximum.

Raman scattering data were obtained on conventional instrumentation. Argon ion, krypton ion, and dye (rhodamine 110 and rhodamine 6G) lasers were used as excitation sources. Power levels were kept at about 5 mW to avoid sample damage. Samples were prepared by slowly depositing a mixture of argon:Br_2:CS_2 (500:1:1) on a polished aluminum cold finger held at 5–10°K. The CS_2 was added to serve as an internal standard to which we could compare the Br_2 intensities. Because the lowest-lying absorption of CS_2 is in the ultraviolet, it shows no resonance effects (other than the ν^4 dependence) for the region we studied.

The resonance Raman spectrum of Br_2 in an argon matrix[9,10] consists of a fundamental at ~315 cm^{-1}, and, as in the gas-phase spectra of halogens,[2,11] a long progression of overtones. In high-resolution spectra, the isotopic splittings may be readily resolved.[10] To obtain the excitation profile we used a spectral slit width of ~4 cm^{-1} passing all three isotopic components while still permitting resolution of the polymer bands occurring at lower frequency (290–305 cm^{-1}). The excitation profile data were obtained by dividing the peak height of the Raman line by the peak height of the CS_2 reference line at 657 cm^{-1}.

The excitation profile of the Br_2 fundamental is presented in Fig. 1 and compared with the absorption profile obtained on the same sample. As in the gas phase, the absorption consists of two overlapping continua with maxima near 20 300 and 24 000 cm^{-1}. These are due to transitions to the B (${}^3\Pi_{0^+u}$) and ${}^1\Pi_{1u}$ states, respectively. Clearly the Raman excitation function bears no obvious relationship to the absorption spectrum. At the low-energy side the Raman re-emission intensity is relatively constant and shows no appreciable enhancement when the laser is tuned through the discrete B (${}^3\Pi_{0^+u}$) levels.[10] As the excitation frequency approaches the strong B-state absorption continuum, the Raman intensity begins to increase rapidly, but it peaks near 18 900 cm^{-1}, far to the

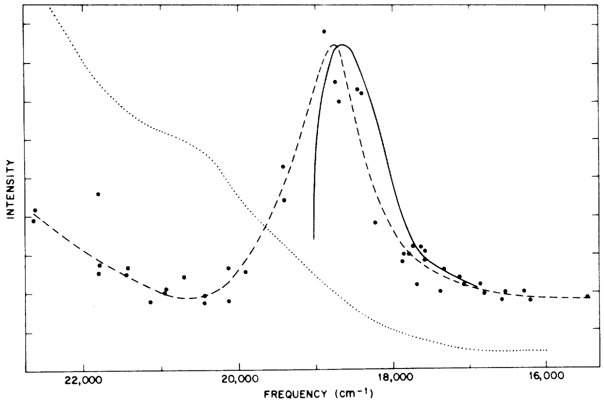

FIG. 1. Excitation profile of the fundamental vibrational mode of Br_2 isolated in a rare-gas matrix. The points are the intensity data of the Raman mode obtained in several experiments. The dashed line is a curve drawn through the data points to guide the eye. The dotted curve is the absorption spectrum; and the solid curve is a calculated excitation profile. The zero of the calculated spectrum was taken as the value of the Raman scattering away from resonance.

red end of the absorption maximum. It then drops sharply and near the B $({}^3\Pi_{0^+u})$ absorption peak it has an intensity similar to the off-resonance value.

To understand the relationship between absorption and scattering data it is necessary to consider the origin of both the absorption and the Raman cross sections. With neglect of terms arising from the coupling between intermediate states through radiative and nonradiative continua, the Raman intensity may be derived from standard second-order perturbation theory:

$$I \propto \alpha \left| \frac{1}{\hbar} \sum_I \frac{V_{FI} V_{IG}}{\omega_{GI} - \omega_L - i\Gamma_I} \right|^2. \tag{1}$$

Since we are dealing solely with resonance processes we have neglected the antiresonance terms in this expression. The matrix elements V_{FI} and V_{IG} correspond to $\langle F|p|I\rangle$ and $\langle I|p|G\rangle$, respectively, for a Raman transition from ground state G to final state F via intermediate state I with width $2\Gamma_I$. The energy of this transition $I \leftarrow G$ is $\hbar\omega_{GI}$ and ω_L is the laser frequency.

If we assume that there is no coupling between states by the laser light field, then we may replace the square of the sum in Eq. (1) by the sum of the squares. By doing this we are assuming that only the resonant state at frequency ω_L contributes to the Raman intensity. We are thereby neglecting possible interference effects and any off-resonance contribution to the Raman scattering. By then replacing the sum by an integral over the density of states we obtain for the Raman intensity

$$I \propto \frac{1}{\hbar} \int d\omega_I \, \frac{V_{FI}{}^2 V_{IG}{}^2}{(\omega_{GI} - \omega_L)^2 + \Gamma_I{}^2} \rho(\omega_I). \tag{2}$$

For $\rho(\omega_I)$ slowly varying relative to a given resonance at ω_L we then obtain

$$I \propto (\hbar\Gamma_I)^{-1} V_{FI}{}^2 V_{IG}{}^2 \rho(\omega_L). \tag{3}$$

Using the Fermi golden rule we may similarly write the absorption coefficient A as

$$A = \hbar^{-1} V_{IG}{}^2 \rho(\omega_L). \tag{4}$$

In comparing Eqs. (3) and (4) the Raman intensity may now be rewritten as

$$I \propto \Gamma_I{}^{-1} A V_{FI}{}^2. \tag{5}$$

We may separate out the vibrational part of the wave functions in the matrix element in Eq. (5) by applying the Born-Oppenheimer approximation. The resulting electronic matrix element $M(\xi)$ is expected to be a weakly varying function of internuclear separation ξ, so that it may be expanded in a rapidly converging series. Substitution of the zeroth-order term of this expansion into Eq. (5) gives

$$I \propto \frac{[M(\xi_0)]^2}{\Gamma_I} A |\langle f | i \rangle|^2. \tag{6}$$

$M(\xi_0)$ is the electronic matrix element evaluated at the equilibrium internuclear separation and the states $|f\rangle$ and $|i\rangle$ now correspond to vibrational wave functions of the ground and excited electronic states, respectively.

By comparing Eq. (4) and (5) [or (6)], the differences between the behavior of the Raman scattering and the absorption may be readily seen. The peak of the absorption is determined by the product of the matrix element times the density of states. It should be noted that for Br_2 gas, under the assumption that the electronic moment is constant, the matrix element V_{IG} connecting $v = 0$ of the X state to the levels of the B state has a maximum near 19 100 cm^{-1}; but the absorption continues to increase beyond this maximum in the region where the matrix element is decreasing. This difference results from the rapidly increasing density of states in this region in spite of the diminished value of the matrix element. However for the Raman scattering as may be seen in Eqs. (5) and (6), the absorption is multiplied by an additional squared matrix element between the B state levels and $v = 1$ of the X state. This matrix element, which is more strongly peaked in the red than that of $v=0$, effectively "overrides" the rapidly increasing density of states in this region below the dissociation limit, thereby causing the Raman excitation profile to reach a maximum towards the red end of the absorption maximum.

The solid line in Fig. 1 is a plot of the excitation profile for the fundamental Raman mode of matrix-isolated Br_2, calculated with use of Eq. (6). Its height was adjusted to correspond to the experimental data. We have assumed that both Γ_I and the electronic matrix element are constant. For the absorption coefficient in this region we used the expression of Seery and Britton[12] evaluated at 0°K, taking into account the 480-cm^{-1} differential shift of the X and B potential surfaces for the matrix-isolated sample compared to the gas.[8] We have neglected the contribution from the $^1\Pi_{1u}$ state which does not absorb in this region. Values for the Franck-Condon factors were taken from the data of Coxon[13] but the energies were also corrected by the 480-cm^{-1} shift.

In view of the approximations made in deriving Eq. (6) we feel that the agreement between the experimental intensity of the excitation profile for the fundamental mode and the calculation presented in Fig. 1 is remarkably good. It is somewhat disturbing, however, that the excitation profile of the overtones cannot be as readily interpreted with this model. Experimentally, as the excitation frequency is moved from the red to the blue the overtones first become observable near 18 000 cm^{-1} and rise in intensity until ~19 500 cm^{-1}, where they reach a constant value. In contrast, the intensity profile calculated for them with use of Eq. (6) predicts an oscillatory behavior due to the variation of the overlap factors.

In view of the overtone results, the approximations made in deriving Eq. (6) should be considered in more detail. We have assumed that the damping factor Γ_I is constant, and that the scattering is dominated by the resonant process. This latter approximation is only rigorously valid for a system in which the linewidths in the intermediate state are smaller than the spacing between the levels, such as the discrete strong absorption region of simple gases. Finally, we have neglected any possible contributions to the intensity from the $^1\Pi_{1u}$ repulsive state.

The damping factor Γ_I for Br_2 in the matrix is certainly varying with the vibrational level of the excited state and must influence our data. However, it should not give the characteristic behavior we observe because in the region of 19 000 cm^{-1} where the Raman intensity starts to decrease the excited-state vibrational spacing is well below the Debye frequency (~75 cm^{-1} for solid argon). Vibrational relaxation occurs through single-phonon processes. Γ_I therefore varies only mildly as a function of energy and cannot account for the abrupt change in Raman intensity that we observe.

By replacing the square of the sum by the sum of the squares in Eq. (1), we are making the assumption that only the resonant part of the excited state contributes to the Raman intensity. This neglects off-resonant contributions from the B state to the scattering intensity as well as any contributions from the $^1\Pi_{1u}$ state. Inclusion of these contributions might smooth out the intensity variation predicted by Eq. (6) for the overtones and make it more consistent with our data, but it could also wash out the sharply peaked profile calculated for the fundamental using the present approximations. However, consideration of the $^1\Pi_{1u}$ state contribution may lead to phase cancellation and reduction in the scattered intensity in certain regions. Indeed some calculations of Raman vibrational intensity distributions recently completed[14] on Br_2 gas in the region of continuum absorption above the convergence limit show substantial interference effects between the B and $^1\Pi_{1u}$ states for the fundamental mode. Such effects could contribute to a red shift in the absorption profile. However, the importance of such effects on the data that we observe may not be quantitatively assessed until a more complete calculation, which is currently in progress, is completed.

Raman excitation profiles are commonly used as a means of studying electronic properties. Yet in a system as simple as Br_2 isolated in an argon lattice, the excitation profile bears no clearcut relationship to the absorption spectrum. We show that a simple model considering only the resonant contribution describes the data for the fundamental vibrational transition reasonably well. Also interference effects between several electronic states may result in Raman intensity profiles whose appearance differs substantially from the absorption spectrum. In view of this, much old data in gases, liquids, solutions, and solids should be re-examined. In general, when a high density of close-lying vibronic states are superimposed or when several close-lying electronic states may contribute to the Raman intensity, detailed numerical analysis must be made to determine the relationship between the absorption and the Raman scattering data. Lacking such analysis, one must exercise the utmost care in attempting to draw conclusions about electronic structure from Raman excitation profile data.

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Propagation and Defocusing of Intense Ion Beams in a Background Plasma*

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The effect of collective interactions between an intense ion beam and a background plasma is found to increase the plasma return current above that necessary for current neutralization, which eventually contributes to defocusing of the beam.

Proposals for replacing high-powered lasers or electron beams in inertial confinement schemes for controlled fusion by intense proton beams[1,2] (~10 MeV) and high-energy (10^2 GeV) heavy ions[3,4] have appeared recently. A critical problem in these proposals is the propagation of the beam from the injector to the target (~10 m distance) in an ambient low-density plasma produced by the previous explosions. In this Letter, we examine the process of current neutralization by the plasma during injection and, in particular, the effect of collective electrostatic interactions on the development of the plasma current. The significance of the magnetic kink mode on such propagation has been examined in an earlier calculation.[5]

It is well known that when a high-powered relativistic electron beam is injected into a plasma, a return current is induced within the beam cross section if the beam radius a exceeds c/ω_e, where ω_e is the electron plasma frequency.[6] This current neutralizes the self-magnetic field of the beam, but it decays after a time $\tau_d \simeq \pi\sigma a^2/c^2$, the magnetic diffusion time, where σ is the plasma conductivity.[7] Plasma currents are also induced when an intense ion beam is injected into a plasma but we show below that, in this case, collective interaction between the beam ions and the background plasma leads to a frictional force which accelerates the plasma electrons. Because of the large momentum of the ion beam, this effect could lead to a return plasma current which actually exceeds the beam current. The resulting reversed magnetic field associated with the net current leads to beam defocusing. The magnitude of this effect is computed below.

Let a well-collimated beam of ions mass m_b, charge $Z_b e$, density n_b, and radius a be injected with velocity w_b into a plasma of electron density n_e, temperature T_e with ion charge Ze. We shall assume that $Zn_e \gg Z_b n_b$ and beam temperature $T_b \ll m_b w_b^2$. The quasilinear equation[8] for the average electron distribution is

$$\frac{\partial}{\partial t}\langle f\rangle - \frac{e}{m_e}E_z\frac{\partial}{\partial v}\langle f\rangle = \frac{\partial}{\partial v}\left(D\frac{\partial}{\partial v}\langle f\rangle\right) + C, \qquad (1)$$

where

$$E_z(r) = \frac{4\pi}{c^2}\frac{\partial}{\partial t}\int_0^r \frac{dr'}{r'}\int_0^{r'} dr''\ r''\ J_t \equiv \left(\frac{4\pi}{c^2}\right)\nabla^{-2}\frac{\partial J_t}{\partial t}$$