PHYSICAL REVIEW B VOLUME 47, NUMBER 21 1 JUNE 1993-I

Asymmetric line shapes and time-resolved measurements: Vibrons in α-$\mathrm{Ar}_x(\mathrm{N}_2)_{1-x}$ mixed crystals

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(Received 23 October 1992; revised manuscript received 3 February 1993)

High-resolution Raman measurements were performed on the $^{14}\mathrm{N}_2$ vibrons and the $^{15}\mathrm{N}_2$ internal vibration in mixed crystals of α-$(^{15}\mathrm{N}_2)_{0.013}(^{14}\mathrm{N}_2)_{0.937}\mathrm{Ar}_{0.05}$. In contrast to what was assumed for the analysis of previous time-resolved coherent anti-Stokes Raman-scattering measurements, asymmetric line shapes are found. We relate the asymmetry to inhomogeneous broadening resulting from perturbations of the perfect lattice structure by the Ar substitution. We discuss the consistency of these frequency-domain results with those of previous time-resolved measurements and finally show how the asymmetry is contained in the time domain.

We have recently performed a time-resolved coherent anti-Stokes Raman-scattering (TR-CARS) study of the dephasing relaxation of the $^{14}\mathrm{N}_2$ vibrons — vibrational excitons — in α-$\mathrm{Ar}_x(\mathrm{N}_2)_{1-x}$ mixed crystals.[1] The TR-CARS signals could be fitted with satisfactory results[1] using the product of an exponential and a Gaussian decay. This decay curve is obtained if a Voigt profile (convolution of a Lorentzian and a Gaussian) is pragmatically assumed in the frequency domain.[2] The characteristic decay time of the exponential function corresponds to the homogeneous (Lorentzian) linewidth in the frequency domain, while the width of the Gaussian decay factor can be related to the inhomogeneous (Gaussian) line broadening. Two $\mathbf{k} \simeq \mathbf{0}$ vibron modes (A_g and T_g symmetry) with a small frequency difference of $\simeq 1\ \mathrm{cm}^{-1}$ are excited by the pump pulse. The resulting beating pattern was described by an additional cosine modulated contribution. This fitting function has been very succesful for the analysis of the decay of the vibrons in pure N_2 crystals and of the $^{15}\mathrm{N}_2$ stretching vibration in the isotopically mixed crystals.[3] Very good agreement was obtained with frequency domain measurements in pure α-N_2.[4,5] Simulations have shown that our fitting method failed[1] for large homogeneous and inhomogeneous line broadening, resulting in an effective decay rate close to the time-resolution (5–7 ps) of the setup.

In this paper, we present high-resolution spontaneous Raman measurements on mixed crystals of α-$(^{15}\mathrm{N}_2)_{0.013}(^{14}\mathrm{N}_2)_{0.937}\mathrm{Ar}_{0.05}$ at 16 K. High resolution was obtained by the use of a Fabry-Perot interferometer to analyze the scattered light.[6] A small concentration of $^{15}\mathrm{N}_2$ molecules was added, allowing us to probe the dynamics of their localized vibrational states. The concentration of the isotopic species was chosen to be sufficiently small in order that the influence on the coupled vibron states is much smaller than that of the 5% Ar doping.[1,3] Comparison of the dephasing of the coupled and isolated states provides direct information on the amount of excitonic character of the coupled vibrations under study.[3,6]

The obtained high-resolution spectrum of the $^{14}\mathrm{N}_2$ vibrons ($\Omega = 2328\ \mathrm{cm}^{-1}$) is shown in Fig. 1. The vibrational line shapes are clearly asymmetric, both for the A_g and the T_g vibron. The line shape for the isolated $^{15}\mathrm{N}_2$ vibrations ($\Omega = 2249\ \mathrm{cm}^{-1}$) is shown in Fig. 2. The line shape is also asymmetric, which clearly shows that the asymmetry of the line shapes is not due to excitonic effects, but is independent of the coupling between the vibrational states. We relate it to differences in local configurations of the N_2 molecules and the Ar atoms. For an Ar concentration of 5%, the probability[7] for dimers of Ar atoms is 24% and for trimers 10.1%. These large probabilities, combined with the mismatch (relative difference: 6%) in lattice parameter, may already cause local distortions of the ideal fcc lattice, shifting the vibrational frequencies slightly, resulting in an asymmetric, inhomogeneously broadened line shape.

In the remainder of this paper, we will address the following questions: (i) Is the information concerning the asymmetry of the line shape also contained in the time-domain dephasing measurements ? (ii) Are the time-domain measurements[1] compatible with the present ones in the frequency domain ?

In transparent materials, applying the Born-Oppenheimer approximation, both spontaneous and stimulated Raman scattering can be described by the nuclear Raman response function:[8]

$$d(t) = \langle [\chi(t), \chi(0)] \rangle , \tag{1}$$

in which χ is the linear optical susceptibility depending parametrically on the nuclear coordinates. The spontaneous Raman spectrum is given by

$$I(\Delta\omega) \propto B(\Delta\omega, T) \int_0^{+\infty} dt \cos(\Delta\omega t) d(t), \tag{2}$$

where $B(\Omega, T)$ is the Boltzmann factor governing the population of the vibrational states (with an energy $\hbar\Omega$) for a given temperature T.

Let us assume an oscillatory function $d(t) = A(t)\exp[i\Omega t + \Phi(t)] + \mathrm{c.c.}$, with Ω the vibrational fre-

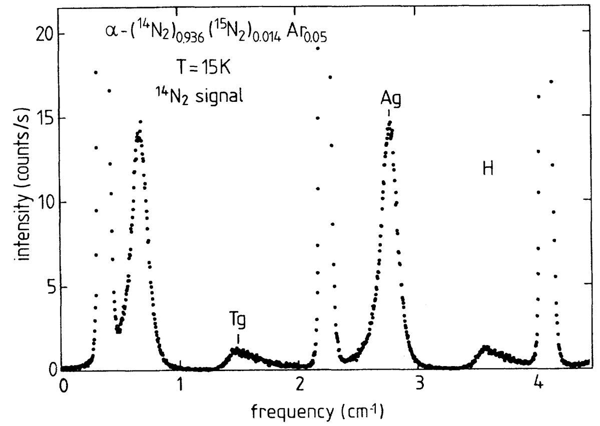

FIG. 1. High-resolution Raman scattering of the $^{14}N_2$ vibrons (Ω = 2328 cm^{-1}) in a mixed crystal of α-$(^{15}N_2)_{0.013}(^{14}N_2)_{0.937}Ar_{0.05}$. The free spectral range (FSR) of the Fabry-Perot interferometer is 1.83 cm^{-1}. The (still present) elastic scattering is about 20 times more intense than the Raman signal. The resolution of our measurements is shown. A_g and T_g modes corresponding to the same order of interference are indicated.

quency, and $A(t)$ and $\Phi(t)$ slowly varying envelope and phase shift functions. Symmetrical and asymmetrical line shapes correspond to $\Phi(t)$ = const and more complicated phase functions, respectively. The pertinent component of the third-order nonlinear susceptibility $\chi^{(3)}$, which governs CARS, is proportional to $d(t)$. Since for the CARS intensity $S_{\text{CARS}}(t) \propto |\chi^{(3)}|^2 \propto |A(t)|^2$,[9] the CARS results are insensitive to the phase $\Phi(t)$, and cannot discriminate symmetrical from asymmetrical line shapes.

Techniques which detect the nonlinear signal in a heterodyne way are capable of measuring at the same time the phase of the signal.[10] One of these is time-resolved stimulated Raman gain (TR-SRG),[11,12] in which the probing process is effectuated by the interaction of the coherent vibration in the sample with a replica of the pump pair. A small portion of the dephasing curve of the ν_1 vibration of CS_2 has already been measured in this way,[10] showing the full potential of this technique.

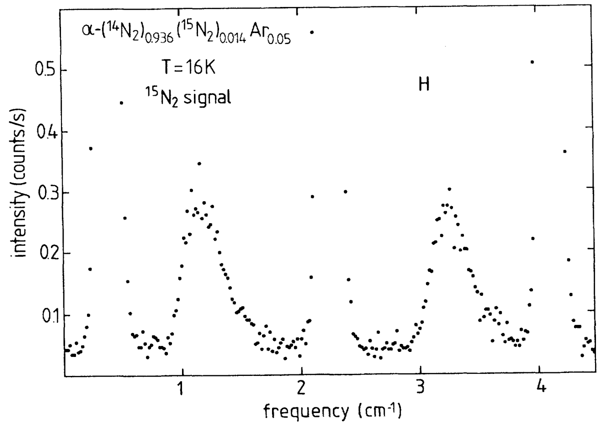

FIG. 2. High-resolution Raman spectrum of the $^{15}N_2$ stretching vibration (Ω = 2249 cm^{-1}) in a α-$(^{15}N_2)_{0.013}(^{14}N_2)_{0.937}Ar_{0.05}$ mixed crystal. The free spectral range (FSR) of the Fabry-Perot interferometer is 1.83 cm^{-1}. The intensity of the elastic scattering is about three orders more intense than the Raman signal. The resolution of our measurements is indicated in the figure.

In order to verify the consistency of our TR-CARS measurements[1] and the high-resolution Raman measurements, we have Fourier transformed the latter. In Fig. 3, the envelope function of the obtained decay curve is plotted together with the obtained TR-CARS decay for the $^{14}N_2$ vibrons in α-$(^{14}N_2)_{0.95}Ar_{0.05}$ mixed crystals (Ref. 1). The comparison between the two techniques suffers on the one hand from the small number of points obtained for $|\chi^{(3)}(t)|^2$ after performing the Fourier transform and on the other hand from the presence of a coherent spike at $t = 0$ in the time-resolved measurements. The latter may be due to electronic contributions to the third-order susceptibility or to instantaneous CARS signals caused by the interaction of one of the pump beams and the probe beam. It remains, however, clear from Fig. 2 that the frequency-domain and the time-domain results are in excellent agreement. Taking the effective decay constant (corresponding to a $1/e$ decay) to characterize the decay, the Fourier transformed curve (70 ± 15 ps) is in good agreement with our TR-CARS measurement (66 ± 5 ps).

This information clearly shows one drawback of the time-resolved measurements: incomplete information is obtained for nonsymmetrical line shapes. Indeed, the assignment to either homogeneous and inhomogeneous line broadening for Ar concentrations $\gtrsim$ 5%, as in Ref. 1, is very doubtful. For α-N_2, no asymmetry in the line shape

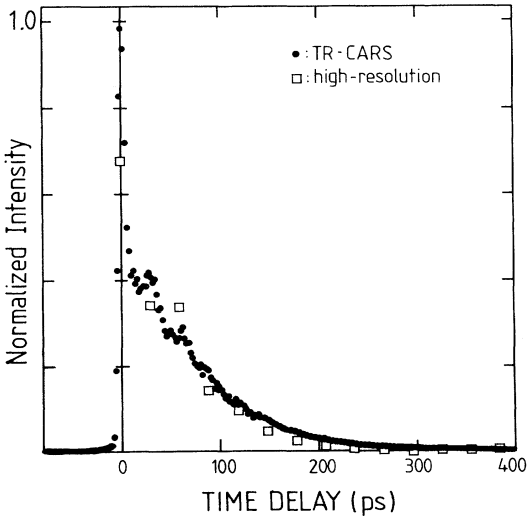

FIG. 3. Fourier transform (□) of the high-resolution spectrum and TR-CARS decay (●, taken from Ref. 1) of the $^{14}N_2$ vibrons in α-$(^{15}N_2)_{0.013}(^{14}N_2)_{0.937}Ar_{0.05}$ and α-$(^{14}N_2)_{0.95}Ar_{0.05}$ mixed crystals, respectively. Both measurements were performed at T = 21 K.

was observed in frequency-domain measurements,[4,5] and this is probably so for low Ar concentrations. Heterodyne measurements have not yet been performed on nontrivial systems and promise to be very difficult, since they neccesitate a very high stability of the optical paths, up to fractions of the wavelength of the light, for long recording times. This paper shows that for complicated systems — having non-Lorentzian line shapes — simple spontaneous Raman measurements may provide more information than elaborate time-resolved experiments.

J.D.K. and E.G. would like to acknowledge financial support from the National Fund for Scientific Research Belgium (NFWO). This work was made possible by further financial support from the Inter-University Institute for Nuclear Sciences (IIKW).

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