Anomalous dependence of the o-D$_2$ roton linewidth on the p-D$_2$ concentration in $(p$-D$_2)_x(o$-D$_2)_{1-x}$ mixed crystals

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High-resolution Raman scattering measurements were performed on the rotons in o-D$_2$, with a varying concentration $0.038 < x < 0.072$ of p-D$_2$. The obtained linewidths are linear in x. Model calculations, which provide excellent agreement for the rotons in p-H$_2$, predict a steeper slope for the D$_2$ case. In contrast to these predictions, a much lower slope is obtained.

In recent years, there has been a renewed interest in the origin of the linewidth of vibrational excitons in molecular crystals.[1] Processes which may lead to line broadening in pure crystals are well documented and the linewidths of optically accessible $\mathbf{k} \simeq \mathbf{0}$ transitions are quite well understood.[1,2] Studies of the linewidth in simple molecular crystals where the $\mathbf{k} \simeq \mathbf{0}$ transition is situated in the middle of the density of states[3–6] and of these transitions in mixed molecular crystals[7–9] are few. In this paper, we present a study of the rotational linewidths in $(p$-D$_2)_x(o$-D$_2)_{1-x}$ mixed crystals. Our results show that this system is not yet understood.

The constraint of symmetry of the nuclear wave function under permutation yields different rotational states for different combinations of nuclear spins, $J = $ even for o-D$_2$ and $J = $ odd for p-D$_2$ molecules. This makes an o-D$_2$ crystal with p-D$_2$ impurities an interesting mixed crystal in which the main perturbation is connected with the rotational properties of the molecules, with all other properties practically unchanged. Quantum rotational excitations on different molecules in o-D$_2$ couple by electric quadrupole-quadrupole (EQQ) interactions to form wavelike excitations which extend throughout the crystal. This interaction also splits the Raman-active transition into three peaks corresponding to $|M| = 0$, 1, and 2 at 176.8, 179.4, and 182.0 cm^{-1},[14,15] respectively. The rotational linewidth in $(p$-D$_2)_x(o$-D$_2)_{1-x}$ mixed crystals has not been studied, while the roton transitions in p-H$_2$ crystals were investigated by high-resolution Raman[6] and time-resolved stimulated Raman gain measurements[4,5] of the corresponding dephasing rate. The obtained linewidths show a linear dependence on the o-H$_2$ ($J = 1$) concentration.

Two model calculations were performed to account for this linear dependence. First, the scattering probability was calculated starting from the Fermi golden rule, assuming that the site of an o-H$_2$ impurity is an empty site for the propagation of the $J = 2$ roton.[10] Good agreement was found for the linear dependence of the $|M| = 0$ and 1 transition, while the slope for the $|M| = 2$ transition was drastically underestimated by more than an order of magnitude. Secondly, a full Green's function calculation was performed, which took also into account the threefold degenerate rotational ground level of the o-H$_2$ impurity. The results of this study are in excellent quantitative agreement with the experimental results.[11]

Later on, the equivalence of doping with o-H$_2$ or with HD molecules showed that the position of the rotational states of the impurity are not important for the scattering rate.[5] As the effective EQQ interaction constant Γ, which governs both calculations,[10,12] changes from 0.575 cm^{-1} for p-H$_2$ to 0.713 cm^{-1} for o-D$_2$, an increase of the scattering rate of about 24% is expected for the o-D$_2$ rotons.

High-resolution Raman scattering measurements were performed using a Fabry-Perot interferometer coupled to a monochromator, which serves as a broad bandpass filter. Further details of the setup can be found in Refs. 7 and 8. As parameters of the system, a finesse $\mathcal{F} = 50$ and a free spectral range of 13 cm^{-1} covering the whole roton band were chosen. This results in a resolution of about 0.26 cm^{-1}. The catalysis of normal D$_2$ to nearly pure o-D$_2$ and the growth of single crystals is analogous to the H$_2$ case and is described in Ref. 4. Single crystals were grown with a concentration of p-D$_2$ varying between 3.8 and 7.2 %. While the lower edge of the concentration
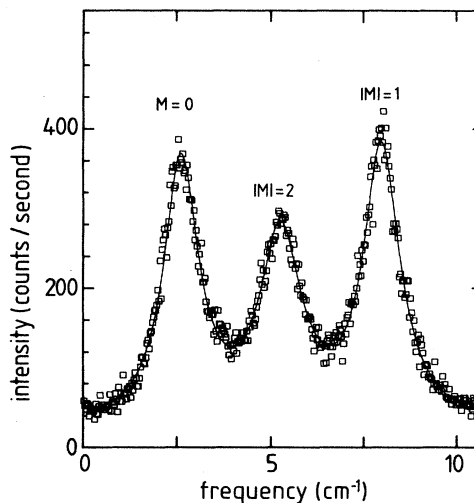

FIG. 1. Experimental Raman spectrum (open squares) and fitting result (solid line) of $J = 0$ to $J = 2$ rotational excitations in $(p$-D$_2)_{0.038}(o$-D$_2)_{0.962}$ mixed crystal. Relative frequency indications were used as the technique does not allow us to perform absolute frequency measurements. The resolution of the experimental setup is 0.28 cm^{-1}, corresponding to a finesse $\mathcal{F} = 50$.
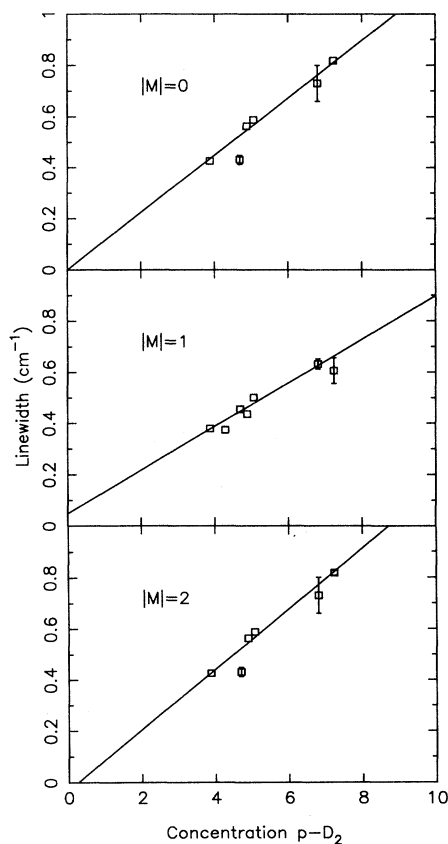
FIG. 2. Experimental linewidth (FWHM) of the roton Raman scattering in o-D_2 as a function of the concentration (given in %) of p-D_2 impurities ($T = 6$ K). Statistical errors from the fitting procedure are indicated only when larger than the symbol size. The full line represent a linear fit to the data points (see also Table I).

TABLE I. Parameters from the linear fit of the roton linewidths as a function of the $J = 1$ concentration.

	Transition	$\Delta\nu$ (cm^{-1}/%)	ν_0 (cm^{-1})
p-H_2[a]	$\lvert M \rvert = 0$	(0.148 ± 0.005)	(0.14 ± 0.01)
	$\lvert M \rvert = 1$	(0.126 ± 0.009)	(0.101 ± 0.009)
	$\lvert M \rvert = 2$	(0.140 ± 0.005)	(0.124 ± 0.005)
o-D_2	$\lvert M \rvert = 0$	(0.084 ± 0.005)	(0.05 ± 0.03)
	$\lvert M \rvert = 1$	(0.085 ± 0.005)	(0.05 ± 0.02)
	$\lvert M \rvert = 2$	(0.112 ± 0.006)	0[b]

[a]Data from Leblans *et al.* (Ref. 5).
[b]Fixed to 0.

range is determined by the smallest p-D_2 concentration that could be obtained by the conversion procedure, a too strong overlapping of the peaks occurs for higher concentrations of p-D_2. The o-D_2 concentration was determined from the intensity of spontaneous Raman scattering off the lowest $\Delta J = 2$ transitions in the liquid phase.[13]

The spectra were analyzed with the individual Raman peaks taken to possess a Lorentzian line shape as a result of lifetime broadening. Therefore a fit was applied involving the convolution of a Lorentzian function with the instrumental resolution function. The latter was derived from the small fraction of elastically scattered light which is still passing the monochromator. As is clear from Fig. 1, a very good fit to the experimental results was obtained, indicating that no inhomogeneous contributions are present in the spectrum. The overlapping of the peaks becomes important at higher p-D_2 concentrations and the peak intensities are decreasing, resulting in a larger uncertainty in the linewidth determination.

The full width at half maximum (FWHM) of the roton transitions are plotted in Fig. 2 as a function of the p-D_2 concentration for the three values of $\lvert M \rvert$. Although the range of p-D_2 concentrations is much smaller than available in the H_2 case, a linear relation between concen-

tration and linewidth may be postulated. The obtained slope $\Delta\nu$ is rather accurate, while the extrapolated value for pure o-D_2, ν_0, could not be determined with a high accuracy. The results for the linear dependence are shown in Fig. 2 and Table I. The latter also contains the fitting results for p-H_2.[5] As can be seen from Fig. 2, an unphysical linewidth $\nu_0 = -0.03$ cm^{-1} results for vanishing $J = 1$ concentration for the $\lvert M \rvert = 2$ transition. To obtain an undisputed value for the slope, we fixed this value at 0, which resulted in a minor change, from 0.118 to 0.112 cm^{-1}/%, of the fitting result. The latter difference was taken as the error on the fitting result.

Table I shows that the obtained slopes for the three values of $\lvert M \rvert$ in solid D_2 are all smaller than for the rotons in solid H_2. This is in clear contrast to the expectations from the model calculations on H_2.[10,12] As the frequency of the rotons in o-D_2 is about half that in p-H_2, a larger contribution of decay in or scattering off lattice phonons may be inferred. However, these processes are less likely, since no temperature dependence was found between 6 K and the melting temperature. In any case, they should result in additional decay channels, yielding larger linewidths. Why smaller values than for solid H_2 are found is not yet understood and is probably related to higher-order terms in the interaction, which could be neglected in the H_2 calculation. The smaller linewidth of the rotons at vanishing p-D_2 concentration is probably due to the stronger EQQ-interaction constant.

The splitting between the $M = 0$ and $\lvert M \rvert = 1$ peak was determined to be 5.25 ± 0.03 cm^{-1}, which is in agreement with 5.2 cm^{-1} (Refs. 14 and 15). No dependence on the $J = 1$ content was found in the small concentration range studied.

In summary, we have performed linewidth measurements on the rotons in $(p$-$D_2)_x(o$-$D_2)_{1-x}$ mixed crystals for $0.038 < x < 0.072$. The linear dependence of the linewidth on the concentration x was found to be in disagreement with the predictions of numerical calculations, although the latter provide good agreement for the corresponding H_2 case. This indicates that a further refinement of the theoretical description is needed.

[1] P. Foggi and V. Schettino, Riv. Nuovo Cimento **15**, 1 (1992).

[2] J. De Kinder, E. Goovaerts, A. Bouwen, and D. Schoemaker, Phys. Rev. B **42**, 5953 (1990).

[3] R. Ouillon, C. Turc, J.-P. Lemaistre, and P. Ranson, J. Chem. Phys. **93**, 3005 (1990).

[4] C. Sierens, A. Bouwen, E. Goovaerts, M. De Mazière, and D. Schoemaker, Phys. Rev. B **37**, 4769 (1988).

[5] M. Leblans, A. Bouwen, C. Sierens, W. Joosen, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **40**, 6674 (1989).

[6] E. Goovaerts, X.Y. Chen, A. Bouwen, and D. Schoemaker, Phys. Rev. Lett. **57**, 479 (1986).

[7] J. De Kinder, A. Bouwen, D. Schoemaker, A. Boukahil, and D.L. Huber, Phys. Rev. B **49**, 12 754 (1994); **49**, 12 762 (1994).

[8] J.L. Feldman, J. Eggert, J. De Kinder, R. Hemley, H.K. Mao, and D. Schoemaker, Phys. Rev. Lett. **74**, 1379 (1995).

[9] J. De Kinder, A. Bouwen, E. Goovaerts, and D. Schoemaker, J. Chem. Phys. **95**, 2269 (1991); Phys. Rev. B **47**, 14 565 (1993).

[10] X.Y. Chen, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **38**, 1450 (1988).

[11] J. Igarashi, J. Phys. Soc. Jpn. **12**, 4586 (1987).

[12] J. Igarashi (private communication).

[13] I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[14] S.S. Bhatnagar, E.J. Allin, and H.L. Welsch, Can. J. Phys. **40**, 9 (1962).

[15] J.P. McTague, I.F. Silvera, and W.N. Hardy, in *Light Scattering in Solids*, edited by M. Balkanski (Hammarion Sciences, Paris (F), 1971), pp. 456–459.