

Relaxation Times of $k = 0$ Rotons in Pure Parahydrogen Crystals and Roton Scattering by Orthohydrogen Impurities

E. Goovaerts, X. Y. Chen,^(a) A. Bouwen, and D. Schoemaker

Department of Physics, University of Antwerp, 2610 Wilrijk-Antwerp, Belgium

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A high-resolution Raman investigation is presented of the linewidth of the $J = 2$ rotons in solid p -H₂ measured by means of a tandem interferometer-monochromator. The magnitude of the linewidths ($\approx 0.08 \text{ cm}^{-1}$) at extremely low o -H₂ concentration is in good agreement with a recent microscopic calculation, but a variation of the experimental widths by a factor of 2 was observed for different $|M_J|$. The dependence of the roton linewidth on the concentration of o -H₂ impurities is found to be linear, indicating that the o -H₂ act as noninteracting random scattering centers.

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The development over the past few years of new time-resolved techniques for the investigation of the relaxation of vibrational and rotational excitations has led to an increased interest in this field.¹ In general, phenomenological equations are introduced to describe the decay of phase and population of the excitation by means of corresponding decay times T_2 and T_1 , giving in many cases a convenient characterization of the observed decay processes. Very recently, a microscopic quantum calculation of the dephasing time, T_2 , was performed for the first time in a molecular solid, i.e., for the Raman-active rotational excitations, called rotons, in solid p -H₂ and o -D₂ (Vanhimebeck *et al.*²). Solid hydrogen is the simplest of molecular crystals and from the large number of available experimental data the isotropic and anisotropic intermolecular potentials are phenomenologically determined to a high precision, while also first-principles calculations yield a quantitatively good description of these potentials.^{3,4} In this interesting model system the lattice vibrations, the rotations, and the intramolecular vibrations are to a high degree decoupled. In spite of its apparent simplicity various nontrivial effects occur among which are phase transitions between different crystalline and orientational phases.³⁻⁵

We have performed very high-resolution linewidth measurements (accuracy $\approx 0.01 \text{ cm}^{-1}$) of the rotational Raman transition (at 355 cm^{-1}) in extremely pure p -H₂, containing to our knowledge the lowest reported o -H₂ concentration, $c_{\text{ortho}} = (0.05 \pm 0.03)\%$. Our results yield a first opportunity for comparison of the theoretical relaxational linewidth, corresponding to the calculated T_2 time,² with experimental data. Furthermore, we have conducted measurements in a series of p -H₂ crystals containing small o -H₂ concentrations: A strongly concentration-dependent line broadening was established which yields the first firm evidence of the scattering of rotons in p -H₂ by o -H₂ impurities.

At zero pressure the solid hydrogens, H₂ and D₂,

crystallize in the hcp structure.³⁻⁵ Because the anisotropic interactions between the molecules are small ($\approx 1 \text{ cm}^{-1}$) compared to their rotational constants ($B = 59.3 \text{ cm}^{-1}$ in p -H₂ and 29.9 cm^{-1} in o -H₂),³ and because the rotational and vibrational coordinates are highly decoupled, the exceptional situation occurs that the molecules behave as weakly perturbed quantum rotators, even in the solid.^{3,4} Because of the constraint of antisymmetry (symmetry) of the molecular wave function under permutation of the protons (deuterons), p -H₂ (o -D₂) can only occur in even J rotational states. In the solid the quantum rotators are subject to anisotropic intermolecular interactions among which the electric quadrupole-quadrupole (EQQ) interaction is dominant.^{3,4} The $J = 0$ to $J = 2$ rotational excitations are coupled together to form traveling-wave excitations, called rotons. The $k \approx 0$ rotons have been investigated earlier by Raman scattering^{6,7}: The spectrum consists of three transitions, split by the EQQ interaction, which correspond to the $|M| = 0, 1,$ and 2 states of the $J = 2$ level. However, the resolution in these early experiments ($\approx 0.3 \text{ cm}^{-1}$) was insufficient to yield significant information about the roton lifetime. Also, no data are available about the dependence of the Raman linewidth on o -H₂ concentration (c_{ortho}) for low amounts of these impurities. In an early calculation⁸ a splitting of 2.25 cm^{-1} between the Raman lines was obtained, to be compared with the experimental value⁶ of 2.0 cm^{-1} . The neglect of phonon renormalization of the EQQ parameter was later shown to be at the origin of this discrepancy.⁹

The recent model calculation² of the T_2 time takes into account single and multiple $J = 2$ excitations, and includes only the EQQ interaction, which is the dominant anisotropic interaction. The results were found to be temperature independent below the melting point (13.8 K for p -H₂) which indicates that the thermal population of rotons is negligible as expected from the high excitation energy, $\Delta E_{\text{rot}}/k_B \approx 510 \text{ K}$ for p -H₂. Also in our experiments in p -H₂ no dependence of the

Raman linewidths was observed in the temperature region from 6 K to the melting point. In contrast to this, a strong dependence on c_{ortho} was found, necessitating great care in the preparation of the p -H₂ samples and in the determination of c_{ortho} .

Gas samples with down to 0.25% o -H₂ impurities were obtained by evaporation of liquid hydrogen (99.9999% H₂ gas as starting material) in contact with an Apachi nickel-silica-gel catalyst³ at 21 K. The purest p -H₂ sample [$c_{\text{ortho}} = (0.05 \pm 0.03)\%$] was produced by subsequent boiling off of the converted liquid at low vapor pressure just below 18 K, and immediate condensation of the gas in the Pyrex sample tube at 15 K. The p -H₂ crystals were grown from the liquid in the Pyrex tube inside an optical helium cryostat, by slow cooling of the bottom tip of the tube. In order to avoid cracks and stresses the crystal was very slowly cooled from the melting point to the measuring temperature (9 K). In this way high-quality p -H₂ single crystals were obtained as testified by visual inspection and by the polarization properties of the Raman spectra. The o -H₂ concentration was determined, both in the liquid before crystal growing and in the solid sample, from the Raman intensity of the $J = 1$ to $J = 3$ transition of o -H₂ relative to that of the Raman-active p -H₂ transition.¹⁰

A few representative high-resolution Raman spectra of the rotors in p -H₂, measured in back scattering, are presented in Fig. 1 for different c_{ortho} . A double monochromator (band pass $\approx 20 \text{ cm}^{-1}$) was tuned to the Raman transition. It was preceded by a double-pass piezoelectrically scanned Fabry-Perot interferometer with a finesse $F \approx 50$ and a free spectral range of 6.3 cm^{-1} , covering the roton Raman spectra. 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 Lorentz function with the instrumental transmission function. The latter was monitored simultaneously with the Raman measurement by the intensity of the elastic scattering detected before the monochromator. At higher c_{ortho} the overlap between the Raman lines becomes more important and the peak intensities are decreasing, resulting in a larger uncertainty in the linewidth determination (Figs. 1 and 2).

The full width at half maximum (FWHM) of the roton Raman lines in p -H₂ has been plotted in Fig. 2 as a function of the o -H₂ concentration. The strong c_{ortho} dependence underlines the need for very pure p -H₂ crystals in order to determine the intrinsic linewidths in this material. The extrapolation to zero concentration (Fig. 2) shows that in our purest sample the widths are mainly intrinsic, i.e., not resulting from the residual amount of o -H₂. The experimental FWHM for the rotors are compared in Table I with the

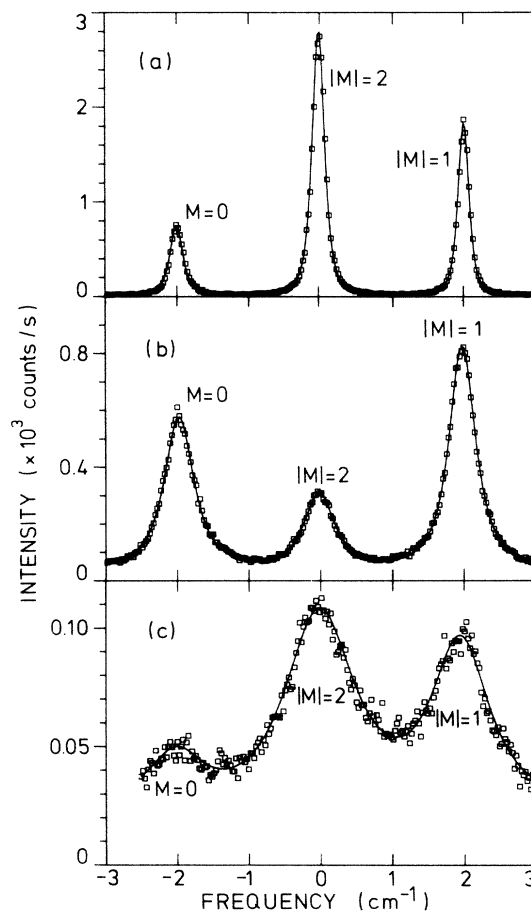


FIG. 1. Experimental Raman spectra (open squares) and fitting result (solid line) of the $J = 0$ to $J = 2$ rotational excitations in p -H₂ (100 mW of Ar⁺ laser excitation at 514.5 nm) measured at $T = 9$ K in single crystals with different concentrations of o -H₂: (a) $c_{\text{ortho}} = (0.05 \pm 0.03)\%$, (b) $c_{\text{ortho}} = (2.6 \pm 0.3)\%$, and (c) $c_{\text{ortho}} = (6.3 \pm 0.6)\%$. The frequency scale is relative to the position of the central peak at 355 cm^{-1} . The relative intensities of the peaks vary from one spectrum to another as a result of different orientations of the crystal with respect to the laser polarization.

theoretical values² resulting solely from the EQQ interaction between the molecules.

The experimental values are seen on the average to be 30% smaller than the theoretical ones. The theoretical linewidths, however, are expected to be reduced mainly as a result of the phonon renormalization of the EQQ interaction parameter,⁹ which would decrease by nearly 20%, while the roton linewidths scale with the square of this parameter.² The resulting close agreement of the average theoretical and experimental values may or may not be fortuitous, because it is difficult to gauge the accuracy of the calculations. However, there is a pronounced difference in experimental linewidth obtained for the three transitions (Table I), which nearly doubles from $|M| = 1$ to $|M| = 0$. Ac-

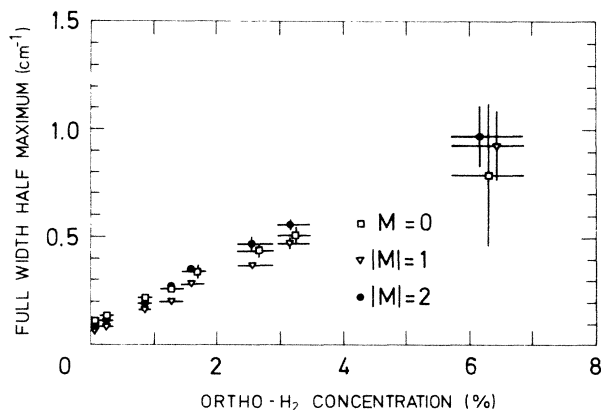


FIG. 2. Experimental linewidth (FWHM) of the roton Raman scattering in p -H₂ as a function of concentration of o -H₂ impurities ($T = 9$ K).

According to the calculation the three peaks possess the same width within 7%, albeit in the same order from narrowest to widest as in the experiment.

Different origins can be put forward to explain this difference: First, the model Hamiltonian may be adequate, but the approximations made may not be valid, either because of neglect of contributions of higher order in the EQQ interaction, or as a result of the truncation of the continued-fraction representation used for the spectral function.² Second, the model Hamiltonian should be augmented with additional anisotropic interactions. This seems less probable in view of the very good results obtained in the description of other rotational properties by consideration of only the EQQ interactions.¹¹ Finally, it is possible that other broadening mechanisms ought to be considered such as phonon-roton interactions. The high-frequency H₂ stretching vibrations (vibrons) were found to possess a much slower relaxation of both population¹² (≈ 10 μ s) and phase (≈ 150 ns in crystals with $c_{\text{ortho}} = 0.22\%$),¹³ and thus are not expected to influence the roton relaxation. It is not excluded, however, that the phonons which possess a much lower frequency [below 120 cm^{-1} in solid H₂ (Ref. 4)] interact with the rotors and contribute to their linewidth. The phonons decay faster than the rotors as is indicated by their larger Raman linewidth (≈ 1 cm^{-1}).¹⁰ One should also pay attention to the possible influence of another impurity, i.e., the hydrogen deuteride molecule which has a natural abundance of 0.03%, comparable to the lowest c_{ortho} in the present experiments. Neither from the present linewidth analysis nor from time-resolved stimulated Raman measurements can one discriminate between these cumulating effects.¹⁴ If, however, one of the additional mechanisms is important it would mean that the calculated linewidth (Table I), resulting from dephasing of the rotors by EQQ coupling only,² is quite strongly overestimated.

TABLE I. Experimental linewidths (in inverse centimeters) of the roton Raman lines in pure p -H₂ [$c_{\text{ortho}} = (0.05 \pm 0.03)\%$] compared to the theoretical values calculated from dephasing of the rotors by the EQQ interaction only (Ref. 2).

	Experiment	Theory
$M = 0$	0.108 ± 0.010	0.119
$ M = 1$	0.062 ± 0.006	0.112
$ M = 2$	0.085 ± 0.006	0.114

Up to now we did not consider inhomogeneous broadening by random strain. One would expect that such an effect would equally broaden the rotors for different $|M|$ values and yield equal linewidths. Also, inhomogeneous broadening would lead to non-Lorentzian line shapes.¹⁴ While for widths much larger than the experimental resolution our fitting procedure is quite sensitive to deviations from this line shape, this is hardly the case for the narrow roton peaks measured in pure p -H₂ samples. Deviations from the Lorentz shape correspond in the time domain to nonexponential decay of the excitation. We plan to investigate this problem by means of T_2 measurements with picosecond time resolution, based on the stimulated Raman scattering effect.¹⁵

A concentration of only a few percent of o -H₂ impurities leads to a tenfold increase of the Raman linewidth of the $J = 2$ rotors. The data shown in Fig. 2 demonstrate that the concentration-dependent contribution to the linewidth is close to linear up to 6% of o -H₂. The broadening results from scattering of the rotors: Indeed, the rotational excitation cannot jump onto the o -H₂ site because of its very different excitation energy. For a single o -H₂ impurity one should then consider the probability of elastic processes in which an incoming Raman-active roton ($k \approx 0$) is scattered into another roton with the same energy, but different wave vector. A large number of such roton states are available since the $k \approx 0$ rotors possess an energy near the center of the $J = 2$ roton band.⁴ The dispersion of the roton energy throughout the Brillouin zone has been evaluated with use of a boson representation of these excitations.¹⁶ The inverse of the total probability per unit of time for the scattering processes yields the roton lifetime. Eventually, inelastic processes, which involve transitions of the o -H₂ impurity within the $J = 1$ rotational level, may also have to be considered. The energy splittings in the ground level of an isolated o -H₂ impurity are much smaller than the width of the $J = 2$ roton band,³ so that the energy transfer can be easily accommodated. If the scattering processes with randomly distributed impurities can be considered as independent, the inverse of the roton lifetime is linear with concentration,^{17,18} and

so is the resulting linewidth. Recently, the dephasing of the $k \approx 0$ vibron in solid p -H₂ was investigated by the time-resolved coherent anti-Stokes Raman spectroscopy technique¹³ for $c_{\text{ortho}} = 0.22\%$ and a few higher concentrations. Also here a strong influence of the o -H₂ impurities was observed, and impurity scattering of the vibrons was put forward. While our Raman spectra at different c_{ortho} give no evidence for nonexponential decay of the rotons, such an effect was clearly seen for the vibrons¹³ in p -H₂.

In conclusion, the present experimental results and the recent microscopic calculation² show that there is a favorable outlook for a fundamental understanding of the relaxational properties of the rotons in p -H₂. Experimentally, time-resolved picosecond experiments can help in discriminating inhomogeneous from homogeneous line broadening. In order to obtain selective information concerning the different processes involved in the roton relaxation, such as roton-roton and roton-phonon interactions, it may be necessary to perform Raman echo experiments.¹⁴ From the theoretical point of view it would be of considerable interest to attempt an evaluation of the phonon contribution to the roton relaxation time. Finally, a calculation of the o -H₂-induced roton relaxation is awaited, either by consideration of a scattering mechanism in the sense described above or, alternatively, in a microscopic approach analogous to the one applied to pure p -H₂ (Ref. 2).

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^(a)Permanent address: Department of Physics, Chongqing University, Chongqing, Sichuan, China.

¹A. Penzkofer, A. Laubereau, and W. Kaiser, *Prog. Quantum Electron.* **6**, 55 (1979); M. J. Burns, W. K. Liu, and A. H. Zewail, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983), p. 301.

²M. Vanhimbeeck, H. De Raedt, A. Lagendijk, and D. Schoemaker, *Phys. Rev. B* **33**, 4264 (1986); the three-digit accuracy of the theoretical linewidths as quoted in Table I was privately communicated.

³I. F. Silvera, *Rev. Mod. Phys.* **52**, 393 (1980).

⁴J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

⁵A. B. Harris and H. Meyer, *Can. J. Phys.* **63**, 3 (1985).

⁶S. S. Bathnagar, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **40**, 9 (1962).

⁷J. P. McTague, I. F. Silvera, and W. N. Hardy, in *Proceedings of the International Conference on Light Scattering in Solids, 1971*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 456.

⁸J. Van Kranendonk, *Can. J. Phys.* **38**, 240 (1960).

⁹J. Noolandi and J. Van Kranendonk, *Can. J. Phys.* **48**, 675 (1970).

¹⁰I. F. Silvera, P. J. Berkhout, and L. M. van Aernsbergen, *J. Low Temp. Phys.* **35**, 611 (1979).

¹¹R. Wijngaarde, L. Lasse, V. Goldman, A. Lagendijk, and I. F. Silvera, unpublished work quoted in Ref. 2.

¹²Chien-Yu Kuo, R. J. Kerl, N. D. Patel, and C. K. N. Patel, *Phys. Rev. Lett.* **53**, 2575 (1984).

¹³I. I. Abram, R. M. Hochstrasser, J. E. Kohl, M. G. Semack, and D. White, *Chem. Phys. Lett.* **71**, 405 (1980).

¹⁴R. F. Lohring and S. Mukamel, *J. Chem. Phys.* **83**, 2116 (1985).

¹⁵M. De Mazière and D. Schoemaker, *J. Appl. Phys.* **58**, 1439 (1985).

¹⁶A. Lagendijk and I. F. Silvera, *Phys. Lett.* **84A**, 28 (1981).

¹⁷C. Ebner and C. C. Sung, *Phys. Rev. B* **2**, 2115 (1970).

¹⁸P. Carruthers, *Rev. Mod. Phys.* **33**, 92 (1961).