Dephasing relaxation of $J = 2$ rotons in parahydrogen crystals doped with hydrogen-deuterium impurities

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The dephasing relaxation times T_2 of the Raman-active $J = 2$ rotons in para-H_2 crystals, intentionally doped with HD impurities, were measured by means of the time-resolved stimulated-Raman-gain (TRSRG) technique. The relaxation rates T_2^{-1} corresponding to the spectral linewidth $\delta v = (\pi T_2)^{-1}$ are found to increase linearly with HD concentration with the slopes 0.148 ± 0.05 cm^{-1}, 0.126 ± 0.05 cm^{-1}, and 0.140 ± 0.05 cm^{-1} per percent for the $|M| = 0$, 1, and 2 rotons, respectively, which, within experimental error, are the same as in the case of ortho-H_2 impurities. This result demonstrates the equivalence of HD and ortho-H_2 for scattering of $J = 2$ rotons in para-H_2. Furthermore the previously suggested possibility that the extrapolated values for the roton relaxation rate in pure para-H_2 would originate from HD impurities at the natural isotope concentration $(c_{HD} \approx 0.03\%)$ is eliminated.

I. INTRODUCTION

During the last few years interesting experimental and theoretical results have been obtained on the dephasing relaxation of the $J = 2$ Raman-active rotons in parahydrogen (para-H_2) crystals.[1-5] Rotons are wavelike excitations consisting of the quantum rotational excitations of the para-H_2 molecules.[6,7] The Raman spectrum of the $J = 2$ rotons in para-H_2 was first measured by Bhatnagar *et al.*[8] It consists of three equidistant lines split by 2 cm^{-1} and centered at 356 cm^{-1}, the transition energy of the free para-H_2 molecule. These Raman lines were found to originate from three zone-center ($\mathbf{k} \approx 0$) rotons, which are even with respect to inversion symmetry and are labeled by the magnetic quantum number $|M| = 1$, 2, and 0, in order of increasing energy.[7] The rotons are well separated in energy from the other excitations in para-H_2, e.g., the crystal phonons (≈ 87 cm^{-1}, $\mathbf{k} \approx 0$ optical phonons),[9] and the intramolecular vibrations that form the so-called vibrons (≈ 4160 cm^{-1}).[6]

Recently, the positions, intensities, and linewidths of the $J = 2$ rotons in para-H_2, and also in orthodeuterium (ortho-D_2), were evaluated in a quantum-mechanical calculation assuming only electric quadrupole-quadrupole (EQQ) interactions between the para-H_2 molecules.[1] In a subsequent high-resolution Raman study in the frequency domain[2] and also from experiments in the time domain[3] using the time-resolved stimulated-Raman-gain (TRSRG) technique,[3,10-13] it was found that the $J = 2$ roton relaxation is strongly dependent on the concentration of ortho-H_2 impurities. From extrapolation to zero impurity concentration the roton relaxation times for pure para-H_2 were determined to be $T_2 = 71$, 102, and 81 ps for the $|M| = 0$, 1, and 2 roton, respectively,[3] and were found to be in reasonable agreement with the theoretical results.[1] As a function of concentration of ortho-H_2 impurities a linear increase was found of the relaxation rates, T_2^{-1}. The latter quantity is proportional to the spectral linewidth, $\delta v = (\pi T_2)^{-1}$. Moreover, the slopes of this linear increase are nearly equal for the three Raman-active $J = 2$ rotons.

Finally, several model calculations were performed ascribing the linear increase of the relaxation rate to scattering of the rotons by the randomly distributed ortho-H_2 impurities. A relatively simple model was proposed in which the ortho-H_2 impurity is considered as an empty site for the propagation of the $J = 2$ rotational excitations, and a golden-rule-type scattering probability was employed.[5] Good results were obtained for the $|M| = 0$ and 1 rotons, but for the $|M| = 2$ roton the calculated scattering efficiency fell short by more than an order of magnitude. Meanwhile, a full Green's-function calculation was performed, taking also into account the threefold degenerate rotational ground level of the ortho-H_2 impurity.[4] The slopes of the relaxation rate versus ortho-H_2 concentration were found to be nearly equal for the three roton transitions and in quantitative agreement with the experiment.

It should be emphasized that para-H_2:ortho-H_2 possesses particularly interesting properties as a defect system. The ortho-H_2 impurity is chemically and isotopically the same as the host molecule. Formally, even the Hamiltonian of the crystal is unchanged, but it is evaluated between different states of the quantum rotator. Indeed, because para-H_2 (ortho-H_2) can exist only in the even (odd) J rotational states[6,7] (see Fig. 1) the lowest rotational excitation energy is $\Delta E_{para} = 6 B_{H_2}$ ($\Delta E_{ortho} = 10 B_{H_2}$), with $B_{H_2} = 59.3$ cm^{-1} (Ref. 6). Due to the very different excitation energies for the two species, the $J = 2$ excitation of the para-H_2 molecule cannot jump onto the ortho-H_2 site. The question was raised whether this is the essential feature which determines the scattering efficiency of the $J = 2$ rotons by the ortho-H_2 impurities, or else whether it is necessary to consider further the properties of this impurity, i.e., its rotational states and excitation energies. Therefore, we have measured the de-
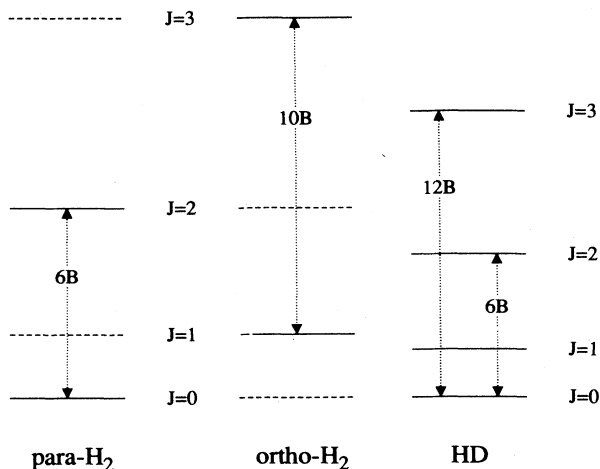
Fig. 1. Energy-level scheme of the low-lying rotational states of the para-H_2, ortho-H_2, and HD molecules, showing the mismatch between the rotational excitations of the different species. The rotational constant B is equal to $B_{H_2} = 59.1$ cm^{-1} for both hydrogen species, and to $B_{HD} = 44.7$ cm^{-1} for the HD molecule.[6]

phasing relaxation of the $J=2$ rotons in para-H_2 crystals which were intentionally doped with HD impurities, taking care to obtain ortho-H_2 concentrations low in comparison to HD. The HD molecule is chemically equal to para-H_2, but isotopically different. It possesses a different moment of inertia $(B_{HD} = 44.7$ cm$^{-1})$[6] and can exist in both even and odd J states of the quantum rotator. The rotational energy spectrum is very different from that of para-H_2 as well as ortho-H_2, which is illustrated in Fig. 1. The results to be presented demonstrate the complete equivalence of ortho-H_2 and HD impurities for roton scattering. They also exclude the possibility suggested earlier,[2,3] that the HD impurities at the natural isotope concentration $(c_{HD} = 0.03\%)$ would be responsible for the relaxation rate determined for the pure para-H_2 crystal by extrapolation to zero ortho-H_2 concentration.

II. EXPERIMENTAL PROCEDURES

The stimulated Raman gain setup employed in the measurements of the roton dephasing times was thoroughly discussed in previous papers.[3,11,13] For decay curves to which a single roton is dominantly contributing, the same procedure for exponential fitting has been applied as in the para-H_2:ortho-H_2 experiments.[3] In many cases a shorter total measuring time was available for experiments in the HD-doped crystals, as will be discussed later, and often it was not possible to measure each of the roton transitions separately. Therefore, an effort was made to determine the T_2 times from decay curves showing a strong beating pattern because two of the roton transitions were involved. This will be described in detail in Sec. III.

The catalysis of normal hydrogen gas to nearly pure

para-H_2 and the growth of single crystals is described in Ref. 3. Small amounts of HD gas were added to the hydrogen gas before the catalysis. Although immediately after growth the crystals were of similar optical quality as the ortho-H_2-doped crystals, their surface became granular after continuous laser illumination, making further TRSRG measurements impossible long before complete sublimation of the crystal. Therefore, the measuring times were limited to about 3 h, and it was not possible in all cases to perform measurements in all the different polarization directions needed to obtain the decay of each of the Raman-active rotons separately.

The impurity concentrations, c_{ortho} and c_{HD}, were determined as in Ref. 3 from the low-temperature spontaneous Raman scattering of the rotational excitations, according to the expressions

$$c_{ortho} = \frac{r(I_{ortho}/I_{para})}{1 + r(I_{ortho}/I_{para}) + s(I_{HD}/I_{para})} \qquad (2.1)$$

and

$$c_{HD} = \frac{r(I_{HD}/I_{para})}{1 + r(I_{ortho}/I_{para}) + s(I_{HD}/I_{para})}, \qquad (2.2)$$

in which I_{ortho} is the integrated intensity of the $J=1$ to 3 transition of ortho-H_2, and I_{para} and I_{HD} are the integrated intensities of the $J=0$ to 2 transition of para-H_2 and HD, respectively. The constant $s=0.987$ is determined by the Stokes shifted frequencies away from the laser frequency (Ar$^+$ at 514.5 nm) only, while the value $r=1.73$ also depends on the matrix elements between rotational states and on the degeneracy of these states. The impurity concentrations have been measured in the liquid, before crystal growth. This procedure was found previously[3] to yield results in good agreement with concentration measurements in the subsequently grown crystal.

III. ANALYSIS OF
BEATING-PATTERN DECAY CURVES

A. Selection of a pair of roton transitions

It is possible to favor strongly the contributions of two roton transitions with respect to the third one, in a way similar to the selection of a single roton transition,[3] by a proper choice of the laser polarizations and of the frequency difference between the two lasers (see Fig. 2). In this selection procedure the conditions on crystal orientation are less stringent than in the single roton selection. In particular, when the hexagonal axis is not lying in a horizontal plane it is not possible to obtain the $|M|=2$ roton separately, while combined signals including this roton can always be selected. Partial data from pure $|M|$ decay curves can then be completed with the fitting results of combined $|M|$ measurements. This is also important, considering the shorter time available for measurements before degradation of the HD-doped para-H_2 crystals.

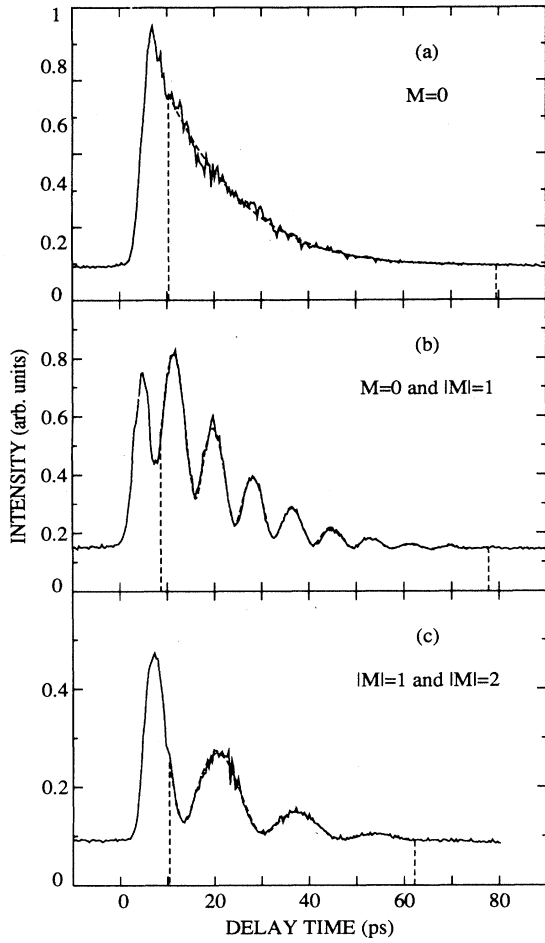When the four laser beams possess the same polarization the contributions of the three transitions are proportional to

FIG. 2. Examples of decay signals of the $J=2$ rotons in para-H_2 at impurity concentrations $c_{HD}=2.35\%$ and $c_{ortho}=0.50\%$, in which (a) only the $M=0$ roton, (b) the $|M|=0$ and 1, and (c) the $|M|=1$ and 2 rotons are contributing. The calculated curve is also shown, as well as the time interval taken into account in the fitting procedure.

$$I_{|M|=0} \sim \tfrac{1}{3}(3\cos^2\theta-1)^2 \ ,$$

$$I_{|M|=1} \sim 4\cos^2\theta\sin^2\theta \ , \qquad (3.1)$$

$$I_{|M|=2} \sim \sin^4\theta \ ,$$

in which θ is the angle between the crystal z axis and the polarization direction.

As soon as the crystal orientation is determined, i.e, for $\theta=0$, the $|M|=0$ transition is selected [Fig. 2(a)]. Simultaneous rotation of all the laser polarizations to $\theta=\cos^{-1}\sqrt{1/3}$ yields comparable contributions of the

$|M|=1$ and $|M|=2$ rotons [Fig. 2(c)]. When all polarizations are perpendicular to the crystal axis only the $M=0$ and $|M|=2$ excitations are selected. This is true even if the crystal axis is vertical, in which case the $|M|=2$ component cannot be separately observed in our setup. In the foregoing cases the wavelength difference between the lasers must obviously be chosen such as to balance the contributions of the two selected rotons. Comparable contributions of $|M|=0$ and $|M|=1$, while eliminating the $|M|=2$ signal, cannot be obtained from the geometrical factors (3.1) only. However, for small θ, the $|M|=0$, $|M|=1$, and $|M|=2$, signals are of zeroth, first, and second order in the angle θ, respectively. A beating decay of the $|M|=0$ and $|M|=1$ rotons with negligible $|M|=2$ contribution can be obtained at small θ, if the frequency difference between the dye lasers is chosen such as to favor the $|M|=1$ transition [Fig. 2(b)].

B. Description and fitting of the beating pattern

Following Ref. 3, the Raman-gain signal from a single roton excitation is a damped oscillation

$$\Delta W(t)=N+A\cos(\omega\tau+\phi)e^{-\tau/T_2} \ , \qquad (3.2)$$

in which $\tau=t-t_0$ is the time delay between the pump pulse at time t_0 and probe pulse at t, ω is the roton frequency, T_2 is its dephasing time, ϕ is a phase factor depending on the optical path length for the laser beams, and N is the noise background originating from electronic components and from the detected laser beam. The constant A contains a geometrical factor determined by the Raman tensor of the roton excitations and the polarization directions relative to the crystal axis. It is also dependent on the frequency difference between the dye lasers, and on their spectral characteristics. As a result of our modulation and alternating current voltage meter (ACVM) detection techniques[3,11] amplitude and phase noise are strongly suppressed and the signal

$$S=(\mathcal{N}^2+\tfrac{1}{2}A^2e^{-2\tau/T_2})^{1/2} \qquad (3.3)$$

is obtained. It combines in a square-root expression the exponentially decaying dephasing signal with $\mathcal{N}$, the high-frequency component of the noise N in (3.2). The latter is found in our setup to be constant and can be eliminated in the analysis of the data. When the three roton transitions are simultaneously contributing (3.2) becomes

$$\Delta W(t)=N+\sum_i A_i\cos(\omega_i\tau+\phi)e^{-\tau/T_2^{(i)}} \qquad (3.4)$$

in which $i=|M|$ labels the parameters A_i, ω_i, and $T_2^{(i)}$ for the different transitions. After noise suppression one gets, instead of (3.3),

$$S=\left[\mathcal{N}^2+\sum_i \tfrac{1}{2}A_i^2e^{-2\tau/T_2^{(i)}}+\sum_i \tfrac{1}{2}A_j A_k\cos(\omega_{jk}\tau)e^{-2\tau/T_2^{(jk)}}\right]^{1/2} \ , \qquad (3.5)$$

in which one must choose $i \neq j \neq k$, and furthermore $\omega_{jk} = \omega_k - \omega_j$ and $1/T_2^{(jk)} = \frac{1}{2}(1/T_2^{(j)} + 1/T_2^{(k)})$.

The beating frequencies ω_{jk} can be directly extracted from the periods of the beating patterns. For each contributing roton excitation two fitting parameters, A_i and $T_2^{(i)}$, have to be included. The instant of zero time delay t_0 must be considered as an additional parameter, since it cannot be directly determined in the experiments. By combining the information from scans in different polarization geometries, and with different laser frequencies, it is in principle possible to assign each T_2 value to the corresponding $|M| = 0$, 1, or 2 roton.

The fitting procedure was tested by means of the earlier measurements[3] of para-H_2:ortho-H_2 crystals, yielding the following conclusions.

(1) An accurate fitting of decay curves with contributions from all three rotons is impossible due to the complicated functional form (3.5) and the large number of independent parameters.

(2) If only two transitions contribute, accurate fitting requires nearly equal contributions of the two rotons, and high quality decay signals. The latter were often hard to obtain as a result of the decreasing optical quality of the crystal in the course of the experiment (Sec. II). Also, the possible occurrence of a small contribution of the third roton transition always had to be considered. Errors on the T_2 times of up to 15% may be produced, above as well as below the correct value. Very few scans yield fitting values which are stable with respect of (i) the time interval taken into account in the fitting procedure, (ii) the subtracted noise background, and (iii) the beating frequency which was introduced as a constant. Only for these scans does the accuracy approach that of the scans in which only one transition is selected.

In many cases the fitting of the beating-pattern decay signals was useful as a double check on the determination of T_2 times from single roton measurements. In the results presented here we have included one fitting result of a beating decay $[|M| = 2, c_{HD} + c_{ortho} = 2.58\%$, Table II and Fig. 3(c)], because this also yields the only reliable measurement made for the $|M| = 2$ roton transition in HD-doped crystals.

C. Energy splitting of the $J=2$ rotons

As a secondary result, the energy splittings between the $|M| = 0$, 1, and 2 components of the roton spectrum are extracted from the dephasing measurements with beating
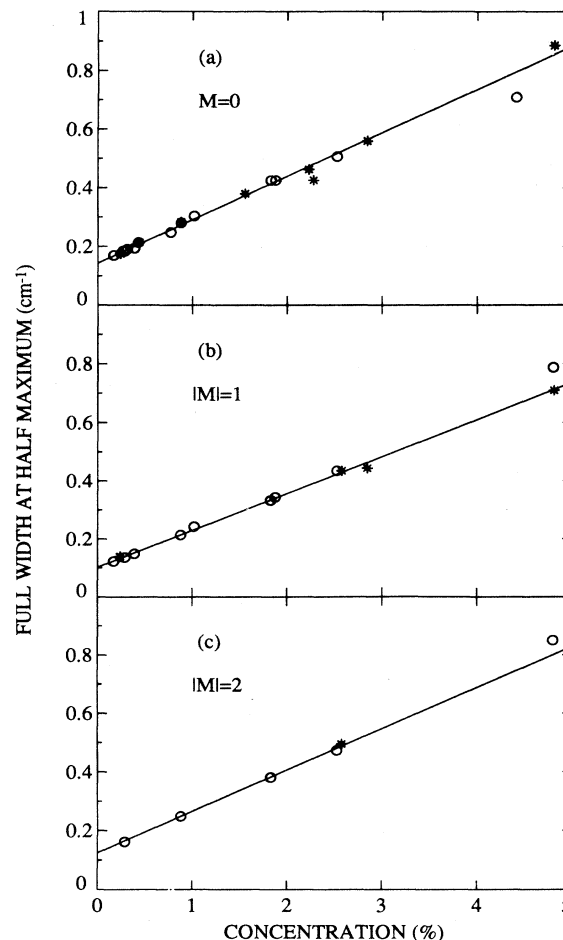

FIG. 3. Full width at half maximum of the $J=2$ roton Raman transitions in para-H_2 as a function of total impurity concentration $c_{HD} + c_{ortho}$. The present results in HD-doped crystals ($*$) are compared with the measurements in crystals containing only ortho-H_2 impurities ($\bigcirc$).

between two roton excitations. Note that three beating frequencies can be extracted from the three possible combinations of two rotons (Sec. III A). As shown in Table I the values obtained from the present TRSRG experiments agree with the original ones of Bhatnagar et al.[8] Values larger by about 5% for these energy splitting were found in recent high-resolution Raman linewidth measurements.[2] However, the absolute accuracy of the latter

TABLE I. Comparison of the energy difference (in cm^{-1}) between the $|M| = 0$, 1, and 2 roton Raman transitions in para-H_2 crystals (a) from the Raman measurements by Bhatnagar et al.,[8] (b) from the recent high-resolution linewidth measurements,[2] both measured in the frequency domain, and (c) from the beating patterns in the time-resolved stimulated-Raman-gain signals (this work).

	(a)	(b)	(c)
ν_{12}	2.01±0.01	2.104±0.016	2.00±0.01
ν_{20}	1.98±0.01	2.055±0.011	1.96±0.02
$\nu_{01}{}^{a}$			3.97±0.03
$\nu_{12} + \nu_{20}$	3.99±0.02	4.16±0.02	3.96±0.02

[a]Direct measurement of $\nu_{01} = \nu_{12} + \nu_{20}$

measurements rely on the calibration of the mirror distance of a Fabry-Perot interferometer, and probably a small error in this calibration has led to systematic errors in the determination of the frequency differences. In the TRSRG measurements errors may arise from measuring the distance between maxima in the beating-pattern decay curves, and from the alignment, calibration, and reliability of the translation stage. The uncertainty in the determination of the maxima results in errors on the energy differences (see Table I) estimated from the spread in values for different time scans and different experiments. Possible systematic errors due to the translation stage have been carefully checked and found to be negligible.

IV. ROTON SCATTERING BY HD IMPURITIES

The T_2 relaxation times of the $J=2$ rotons have been measured in a series of para-H_2 crystals with impurity (HD and ortho-H_2) concentration ranging from 0.24% to nearly 5%. In all of these crystals the HD concentration was at least three times larger than the ortho-H_2 concentration. The T_2 time was converted to the corresponding full width at half maximum (FWHM) in the frequency domain, $\delta\nu = 1/\pi T_2$, and is shown in Fig. 3 as a function of total impurity concentration, including both HD and ortho-H_2. The results obtained in para-H_2 crystals with only ortho-H_2 impurities[3] are also included for comparison. For the $|M|=0$ and 1 rotons the two sets of data show very closely the same linear increase of the linewidth with impurity concentration. A separate analysis was performed on the new sets of data on the basis, either of a single linear dependence on the total impurity concentration, or of a multilinear dependence on c_{ortho} and c_{HD}. In all cases the slope of the FWHM as a function of these variables, as well as the extrapolated value for pure para-H_2, were found to be equal to the results from ortho-H_2 impurities,[3] within experimental accuracy. Due to the experimental difficulties described earlier, for the $|M|=2$ roton only one significant measurement at $c_{\text{HD}}=2.51\%$ and $c_{\text{ortho}}=0.07\%$ has been obtained. As seen in Fig. 3(c), also this measurement is consistent with the data obtained from the para-H_2:ortho-H_2 system. The extrapolated linewidth for pure para-H_2 crystals and the slopes, determined from the total set of data presented in Table II and Fig. 3, are given in Table III.

First, we can exclude on this basis the possibility mentioned in Ref. 2 that the HD impurities at natural isotopic concentration would cause the dephasing of the rotons in pure para-H_2 crystals, as found from extrapolation to zero impurity concentration. In that case the HD molecules would have needed a much higher scattering efficiency for $J=2$ rotons. In pure crystals the EQQ interactions between the molecules,[1] or else roton-phonon interactions, have to be invoked. Inhomogeneous broadening mechanisms seem to be less probable because of the exponential form demonstrated for the roton decay.[3]

TABLE II. Detailed list of the experiments concerning the dephasing of $J=2$ rotons in para-H_2 crystals with orth-H_2 and HD impurities, showing the impurity concentrations and the resulting T_2 times for the three roton transitions.

Concentration (%)				T_2 times (ps)	
ortho-H_2	HD	total	$M=0$	$|M|=1$	$|M|=2$
0.14	0.03	0.17	63 ± 2[a]	88 ± 3[a]	
0.08	0.16	0.24	61 ± 2	77 ± 3	
0.24	0.03	0.27	58 ± 2[a]		
0.26	0.03	0.29	58 ± 2[a]	79 ± 5[a]	66 ± 2[a]
0.28	0.03	0.31	56 ± 2[a]		
0.36	0.03	0.39	55 ± 2[a]	72 ± 3[a]	
0.40	0.03	0.43	50 ± 2		
0.13	0.31	0.44	50 ± 2		
0.74	0.03	0.77	43 ± 2		
0.85	0.03	0.88	38 ± 1[a]	50 ± 2[a]	43 ± 3[a]
0.62	0.26	0.88	38 ± 1		
0.99	0.03	1.02	35 ± 1[a]	44 ± 2[a]	
0.06	1.50	1.56	28 ± 1		
1.80	0.03	1.83	25 ± 2[a]	32 ± 2[a]	28 ± 2[a]
1.85	0.03	1.88	25 ± 1[a]	31 ± 2[a]	
0.16	2.07	2.23	23 ± 2		
0.77	1.51	2.28	25 ± 2		
2.50	0.03	2.53	21 ± 1[a]	25 ± 1[a]	23 ± 1[a]
0.07	2.51	2.58		24.5 ± 0.5[b]	21.5 ± 0.5[b]
0.50	2.35	2.85	19 ± 1	25 ± 1	
4.38	0.03	4.41	15 ± 1[a]		
4.77	0.03	4.80		13.5 ± 0.5[a]	13 ± 1[a]
0.63	4.18	4.81	12 ± 1	15 ± 1	

[a]From Ref. 3.
[b]From beating-pattern decay curves.

TABLE III. The extrapolated linewidths, δv_0, for the pure para-H_2 crystal of the $|M|=0$, 1, and 2 roton Raman transitions and the increase per percent of the linewidth, $\Delta(\delta v)$, both in cm^{-1}, derived from the complete set of experiments in crystals with ortho-H_2 and HD impurities (Table II).

	$M=0$	$|M|=1$	$|M|=2$
δv_0	0.14±0.01	0.101±0.009	0.124±0.005
$\Delta(\delta v)$	0.148±0.005	0.126±0.005	0.140±0.005

Second, we conclude that HD impurities have the same influence on the relaxation rate of the $J=2$ rotons in para-H_2 as the ortho-H_2 impurities. From the point of view of scattering of the rotons by these impurities,[4,5] this means that the scattering probabilities are not influenced by the details of the rotational states and excitation energies, which are very different for the ortho-H_2 and HD species. The essential point is that the excitation energies of the impurity molecules do not match the energy of the $J=2$ rotons of the host crystal. In fact the impurity can be considered as an empty site in the crystal with respect to the propagation of the $J=2$ rotational excitations, as was assumed in the model calculation of Ref. 5. In this calculation, however, the scattering probabilities were calculated in a golden-rule approximation, which was found to yield reasonable agreement with the experimental results for the $|M|=0$ and 1 rotons, but falls short by more than an order of magnitude for the $|M|=2$ roton. Probably, this would be overcome by applying scattering theory to higher order in a Green's-function approach as was done in Ref. 4. In the latter calculation a very good agreement with experiment[3] was obtained. Unfortunately, the assumed model is specific for the internal rotational structure of the ortho-H_2 impurity, and the result cannot be simply transposed to the roton scattering by HD molecules.

ACKNOWLEDGMENTS

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