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Double transitions in the Raman spectrum of the fundamental band of solid parahydrogen

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In this paper we report the observation of double Raman transitions of the type $Q_1(0)+S_0(0)$ in the fundamental band of solid parahydrogen. Although this band is a forbidden one, its intensity is of the order of 20% of the corresponding allowed $S_1(0)$ band. The reason for this unusual behavior is discussed in some detail and is attributed to the strong mixing of the final states in the two manifolds involved.

I. INTRODUCTION

In a recent paper by Baliga *et al.*,[1] double Raman transitions in the fundamental band of solid D_2 were reported and briefly discussed. It was found that the intensity of the forbidden double transitions in the $Q_1(J)+S_0(0)$ band was of the same order of magnitude as that of the allowed $S_1(0)$ band. A similar situation should exist in H_2. There are a number of reasons that make H_2 more suitable for the investigation of this effect than D_2. In the first place, the double and single transitions are well separated in frequency and allow a reliable determination of these two intensities independently. In the second place, the intensity of the double transition in H_2 is expected to be weaker than in D_2 and can therefore be discussed in terms of perturbation theory. Finally, because H_2 is softer, it is easier to investigate the density dependence of the effect. It was suggested in Ref. 1 that this phenomenon is due to mixing of states from the $S_1(0)$ manifold with those from the $Q_1(0)+S_0(0)$ manifold. The energy difference, ΔE, between the unperturbed states in these manifolds is 6 and 18 cm^{-1} in D_2 and H_2, respectively. Because these energy differences are of the same order of magnitude as the electric quadrupole-quadrupole interaction which connects these manifolds, very strong coupling will occur and the forbidden-double-transition intensity can be appreciable as compared to that of the allowed $S_1(0)$. This is in contrast to previously observed double transitions of the type $S_0(J)+S_0(J')$ by Berkhout and Silvera,[2] where ΔE is much larger than the corresponding interaction strength, and where therefore the double-transition intensity is of the order of 0.1% of the allowed one.

It is of interest to note that in absorption both the $S_1(0)$ and the $Q_1(0)+S_0(0)$ dipole transitions are forbidden for homonuclear diatomic molecules. Both of these are observed because of the existence of induced dipoles in pairs of molecules.[3] In the Raman case, there is also a contribution from induced polarizability, but the associated intensity is much weaker than the one with which we are concerned here.

In Sec. II we discuss the theory of the mixing of states in terms of perturbation theory and obtain expressions for the integrated intensities of the $Q_1(0)+S_0(0)$, $S_1(0)$, and $Q_1(0)$ bands. In Sec. III we describe the experimental procedure and apparatus and in Sec. IV we present the experimental results together with a comparison with theory.

II. THEORY OF THE INTENSITY OF THE DOUBLE TRANSITIONS

Double Raman transitions can occur as a result of two different mechanisms. The first of these mechanisms is connected with the existence of interaction-induced polarizability in which, for example, the irreducible components of the polarizability tensor of a pair of molecules contain terms of the type $\alpha_{lm}(\mathbf{r}_1\mathbf{r}_2\mathbf{R})$ where $\mathbf{r}_1=(r_1,\Omega_1)$ and $\mathbf{r}_2=(r_2,\Omega_2)$ refer to the internuclear distances and orientations of the molecules and $\mathbf{R}=(R,\Omega)$ to the separation of the centers of mass in a space-fixed coordinate system.

The polarizability of a pair of molecules, labeled 1 and 2, can therefore be written in the form

$$\alpha_{lm}(\mathbf{r}_1\mathbf{r}_2\mathbf{R})=\alpha_{lm}^{(1)}(\mathbf{r}_1)+\alpha_{lm}^{(2)}(\mathbf{r}_2)+\alpha_{lm}^{(\text{ind})}(\mathbf{r}_1\mathbf{r}_2\mathbf{R}) , \qquad (1)$$

where $\alpha_{lm}^{(1)}$ is the polarizability tensor of the isolated molecule 1 and similarly for molecule 2. The term $\alpha_{lm}^{(\text{ind})}$ describes the induced, or incremental, polarizability which arises from the intermolecular interaction. The allowed polarizability tensors for a diatomic molecule, referred to a space fixed frame, are given by[4]

$$\begin{aligned} \alpha_{00}^{(1)} &= -\sqrt{3}\alpha(r_1) , \\ \alpha_{2m}^{(1)} &= \sqrt{8\pi/15}\gamma(r_1)Y_{2m}(\Omega_1) , \end{aligned} \tag{2}$$

where $\alpha(r_1)=[\alpha_{\parallel}(r_1)+2\alpha_{\perp}(r_1)]/3$ is the isotropic polarizability of molecule 1 as a function of internuclear distance r_1; $\gamma(r_1)=\alpha_{\parallel}(r_1)-\alpha_{\perp}(r_1)$ is the corresponding anisotropy and $Y_{2m}(\Omega_1)$ refers to a spherical harmonic with argument $\Omega_1\equiv(\theta_1,\phi_1)$ referred to space fixed axes. The dominant contribution to the induced polarizability comes from the dipole–induced-dipole (DID) mechanism. There are several contributions of this type which are all proportional to terms of the form $\alpha_{lm}^{(1)}\alpha_{l'm'}^{(2)}R^{-3}$ where $l,l'=0,2$. This means that the matrix elements of the induced polarizability differ from the allowed ones by factors of order $\alpha/R^3\approx(a_0/R)^3\approx10^{-2}$, where a_0 denotes the first Bohr radius. The intensity due to induced Raman scattering is therefore quite small compared to that of the allowed, although such transitions have previously been observed.[2]

The second mechanism giving rise to double transitions is due to the mixing of states. In the experiment discussed in this paper we are interested in single transitions of type $S_1(0)$ and double transitions of type $Q_1(0)+S_0(0)$. The unperturbed states in the $S_1(0)$ manifold are those in which one molecule, which we will refer to as the central molecule, is in a vibrational state $v=1$ and has rotational quantum numbers (J,M) with $J=2$. We will denote these states by $|2,M\rangle_0$. The unperturbed state of the $Q_1(0)$ manifold, in which the central molecule is in the state $v=1$, $J=0$, $M=0$ is denoted by $|0,0\rangle_0$. The unperturbed states of the $Q_1(0)+S_0(0)$ manifold are those in which the central molecule is in the $v=1$, $J=0$ state and in which one of the neighboring molecules, referred to as the jth molecule, is in the rotational state $(2,m)$. These states will be denoted by $|2_j,m\rangle_0$.

In the independent-polarizability approximation (IPA), single transitions of the type $Q_1(0)$ and $S_1(0)$ take place between unperturbed states. The corresponding integrated scattering intensities in the crystal (number of photons per unit time, per unit solid angle and per unit scattering volume) are given by

$$\begin{aligned} I^{IJ}[Q_1(0)] &= \frac{\omega_0\omega_s^3}{c^4}n_0\rho\,|\langle 0|\alpha_{IJ}|0,0\rangle_0|^2 , \\ I^{IJ}[S_1(0)] &= \frac{\omega_0\omega_s^3}{c^4}n_0\rho\sum_M|\langle 0|\alpha_{IJ}|2,M\rangle_0|^2 , \end{aligned} \tag{3}$$

where ω_0 and ω_s are the incoming and scattered frequencies, c is the velocity of light, n_0 the number of incoming photons per unit time and unit area, ρ the density of the crystal, α_{IJ} is the Cartesian component of the polarizability tensor of a single molecule in the laboratory frame $(I,J=x,y,z)$, and $|0\rangle$ is the ground state of the crystal. In the IPA, double transitions to the unperturbed states mentioned above do not occur. If mixing of states takes place intensity will appear in the $Q_1(0)+S_0(0)$ double transition and, because of the principle of spectroscopic stability, an equal amount of intensity will be removed from the $S_1(0)$ transition.

It is well known that the dominant anisotropic interaction between hydrogen molecules is the electric quadrupole-quadrupole (EQQ) interaction.[4] This interaction couples the $S_1(0)$ and $Q_1(0)+S_0(0)$ manifolds and is therefore expected to give rise to the mixing of states and the resulting double transitions. For pure rotational Raman scattering, the mixing of states is small and gives rise to an intensity of double transitions which is of the same order of magnitude as that associated with the induced polarizability. In the present case of the fundamental band the mixing is very strong because the energy difference between the unperturbed states is ≈18 cm^{-1} and of the same order of magnitude as the EQQ interaction. Therefore the intensity of the double transitions turns out to be only 1 order of magnitude less than that of the allowed one. We take the point of view that the vibrational excitation is localized on a single molecule. This means that we neglect the vibrational hopping interaction which gives rise to a rather narrow vibrational energy band which has no appreciable influence on the integrated intensity of the transition. To estimate the magnitude of the effect of mixing on the intensity we can, for the case of H_2, use perturbation theory and write for the perturbed states in the $Q_1(0)+S_0(0)$ manifold

$$|2_j,m\rangle=|2_j,m\rangle_0+\sum_M a_{Mm}^j|2,M\rangle_0 , \tag{4}$$

where a_{Mm}^j is the matrix element of the EQQ interaction between the central and the jth molecule, divided by the appropriate energy separation ΔE, and is given by

$$\begin{aligned} a_{Mm}^j &= \langle 2,M|V_{\mathrm{EQQ}}|2_j,m\rangle_0/\Delta E \\ &= \lambda(4\pi)^{1/2}C(242;M,m-M,m) \\ &\quad\times(R_0/R_j)^5Y_{4,m-M}(\Omega_j) . \end{aligned} \tag{5}$$

The perturbation parameter λ is given by

$$\lambda=\frac{\sqrt{14}\langle 00|Q|02\rangle\langle 10|Q|12\rangle}{5\,\Delta E\,R_0^5} . \tag{6}$$

In these expressions C denotes a Clebsch-Gordan coefficient, R_0 is the equilibrium lattice spacing, and R_j the separation between the jth and the central molecule. The z axis of the space fixed coordinate system is used as the quantization axis; the orientation of the molecules, Ω_j, is with reference to the c axis of the hcp lattice which, in turn, is also taken along the space-fixed z direction. The matrix elements of the quadrupole moment between vibrational states, which have a minor J dependence because of rotation-vibration interaction, are denoted in Eq. (6) by $\langle vJ|Q|v'J'\rangle$. They are well known from *ab initio* calculations. The perturbation parameter λ turns out to be $\lambda=0.127$ in the case of H_2 as discussed in more detail in the next section. Because the mixing coefficients a_{Mm}^j, like the EQQ interaction, are proportional to R^{-5}, the mixing takes place mainly with the nearest neighbors of the central molecule and we will neglect the effect of all other molecules. The integrated intensity of the double transitions is given by the sum over final states in the $Q_1(0)+S_0(0)$ manifold of the polarizability matrix elements

$$I^{IJ}[Q_1(0)+S_0(0)]=\frac{\omega_0\omega_s^3}{c^4}n_0\rho\sum_{j,m}|\langle 0|\alpha_{IJ}|2_j,m\rangle|^2 . \tag{7}$$

The components α_{IJ} can be expressed in a straightforward way in terms of the α_{lm} given in Eq. (2).[4] It is clear that the EQQ interaction also mixes the states $|2_j,m\rangle_0$ for different values of j among themselves. This mixing does not produce any further intensity in the $Q_1(0)+S_0(0)$ band and we therefore do not take it into account. In a similar way, the crystal fields, although they affect the shape of the band, do not contribute to the integrated intensity of the double transitions and are not considered. Upon substitution of Eq. (4) into Eq. (7) the integrated Raman intensity of the double transitions takes the form

$$\begin{aligned}I^{IJ}&[Q_1(0)+S_0(0)]\\&=\frac{\omega_0\omega_s^3}{c^4}n_0\rho\sum_{M,M'}\left[\sum_{j,m}a^j_{Mm}a^{j*}_{M'm}\right]\langle 0|\alpha_{IJ}|2,M\rangle_0\\&\qquad\times\langle 0|\alpha_{IJ}|2,M'\rangle_0^* .\end{aligned} \tag{8}$$

The quantity in large parentheses is given by

$$\begin{aligned}\sum_{j,m}&a^j_{Mm}a^{j*}_{M'm}\\&=\lambda^2\sum_l(2l+1)C(4l4;00)\\&\qquad\times\sqrt{45}W(2244;l2)C(2l2;M,M'-M,M')\\&\qquad\times\sum_j(R_0/R_j)^{10}\left[\frac{4\pi}{2l+1}\right]^{1/2}Y_{l,M'-M}(\Omega_j) ,\end{aligned} \tag{9}$$

where W denotes a Racah coefficient and the sum over l involves $l=0,2,4$. It follows from the hcp crystal symmetry that the sums over j which occur in Eq. (9), are only different from zero for $M=M'$; and for the same reason there is no contribution from $l=2$. Therefore, Eq. (8) becomes

$$\begin{aligned}I^{IJ}&[Q_1(0)+S_0(0)]\\&=\frac{\omega_0\omega_s^3}{c^4}n_0\rho\sum_M\left[\sum_{j,m}|a^j_{Mm}|^2\right]|\langle 0|\alpha_{IJ}|2,M\rangle_0|^2 .\end{aligned} \tag{10}$$

The main contribution to the quantity in large parentheses corresponds to $l=0$ in Eq. (9) and is of magnitude $12\lambda^2$. It corresponds to approximating the lattice sum in Eq. (9) by an integration over all directions, i.e., it describes the part of the scattering that is independent of the orientation of the crystal. The effects of crystal orientation are incorporated in the M-dependent contribution, associated with $l=4$, to $\sum_{j,m}|a^j_{Mm}|^2$; they are found to be of order 10% and will not be considered at this time because they are of the same order of magnitude as the present experimental uncertainty. With this approximation, it is clear from Eqs. (3) and (10) that the intensity ratio of double to single transitions is $12\lambda^2$.

We now want to consider two points of detail in the calculation. The first point concerns the influence of the lattice vibrations on our result. It is clear that the quantities a^j_{Mm} are really expectation values over the ground state of the lattice and should be phonon-renormalized.[4] For the EQQ interaction this can be accomplished approximately by introducing an effective EQQ interaction between molecules 1 and 2 of the form

$$V^{\text{eff}}_{\text{EQQ}}=\xi_{54}V_{\text{EQQ}}(\Omega_1\Omega_2R_0) , \tag{11}$$

in which the interaction on the right-hand side refers to a rigid lattice. The scaling parameter ξ_{54} is discussed in some detail in the literature.[4,5] The result is that, in our calculation, the ratio of double to single transitions should be multiplied by ξ_{54}^2 to correct for lattice vibrations.

As a second point of detail, we consider the normalization of the first-order wave functions. Because this is an effect of order λ^2, it is usually not taken into account in perturbation calculations. In fact, the proper normalization factor for the states in Eq. (4) is approximately given by $(1+\lambda^2)^{-1/2}$ and we should therefore replace λ in the previous calculation by $\lambda/(1+\lambda^2)^{1/2}$. Considering that $\lambda\approx 0.1$, this correction is negligible. The effect of normalization on the unperturbed $S_1(0)$ intensity given in Eq. (3) is not negligible however. This is due to the fact that the states $|2,M\rangle_0$ of the central molecule mix with those of all its 12 neighbors and this implies that the normalization factor for the perturbed $|2,M\rangle$ state is given approximately by $(1+12\lambda^2)^{-1/2}$. The unperturbed $S_1(0)$ intensity given in Eq. (3) should therefore be divided by $1+12\lambda^2$ to account for normalization. Note that this reduction of the $S_1(0)$ intensity is, as expected, just equal to the double transition intensity calculated above. Finally, for the ratio of double to single transitions we therefore find

$$\frac{I^{IJ}[Q_1(0)+S_0(0)]}{I^{IJ}[S_1(0)]}=\xi_{54}^2 12\lambda^2(1+12\lambda^2) . \tag{12}$$

III. EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental light-scattering apparatus is a conventional one and consists of an argon-ion laser operating at a wavelength of 4880 Å, a double monochromator, and a photon-counting system connected to a computer. Concerning this apparatus, a new photomultiplier, a Varian VPM-164S cooled at $T=-40\,^{\circ}\mathrm{C}$, is worth mentioning. It has a dark noise-counting rate of 0.07 counts/s together with a higher efficiency, as compared to the usual photomultiplier. This decreased our detection time by a factor ≈ 2.5 as compared to our previous system.[6] The spectral response of our detection system, double-monochromator plus photomultiplier, has been

TABLE I. Experimental and theoretical values of the intensity ratios in the vertical geometry (denoted by $I_V=I^{xx}+I^{xz}$) for the various transitions. Here $I_V[S_1(\mathrm{tot})]$ denotes the intensity of the $S_1(0)$ plus the $S_0(0)+Q_1(0)$ transitions. The theoretical values a refer to $\xi_{54}=0.856$, while b refers to $\xi_{54}=0.942$. The density at zero pressure is $\rho_0=42.9$ mol/l (Ref. 8).

				$\frac{I_V[S_0(0)+Q_1(0)]}{I_V[S_1(0)]}$			
T	P	ρ			Theor.		$\frac{I_V[S_1(\mathrm{tot})]}{I_V[Q_1(0)]}$
(K)	(bars)	(mol/l)	ρ/ρ_0	Expt.	a	b	Expt.
18.5±0.5	244±0.5	46.7±0.3	1.09±0.01	0.225±0.02	0.22	0.27	0.103±0.015
17±0.5	241±0.5	47.8±0.3	1.11±0.01	0.208±0.02	0.24	0.29	0.095±0.015
15±0.5	244±0.5	48.4±0.3	1.13±0.01	0.240±0.02	0.25	0.31	0.109±0.015

carefully calibrated with a halogen light source with tungsten filament model No. 245A calibrated by Optronic Lab. Inc. on the basis of a National Bureau of Standards standard, with an overall precision of 1.5%. This calibration was performed over a range of 5000 cm^{-1} on the Stokes side of the laser exciting line using light vertically or horizontally polarized with respect to the direction of the grating's grooves. This is of great importance for the comparison of the intensities of the various features of the spectrum of the scattered radiation. The high-pressure scattering cell is similar to the one described in Ref. 7 but with a larger internal volume, approximately 1 cm^3, which permitted the insertion of some Cr_2O_3-γ-Al_2O_3 as a catalyst into the cell. This was used to increase the rate of conversion from orthohydrogen to parahydrogen at low temperature in the liquid phase. The parahydrogen was directly produced by filling the scattering cell with the liquid at $T\approx22$ K at a pressure $p\approx250$ bars and creating convection in order to increase the exchange contact between the liquid and the catalyst. The parahydrogen concentration was monitored by measuring the ratio between the rotational $S_0(0)$ and $S_0(1)$ lines according to the expression[8]

$$x_p=\frac{I[S_0(0)]/I[S_0(1)]}{\dfrac{I[S_0(0)]}{I[S_0(1)]}+\dfrac{5}{3}\left[\dfrac{\omega_L-\omega_0}{\omega_L-\omega_1}\right]^3}\,, \tag{13}$$

where x_p is the parahydrogen concentration, $I[S_0(0)]$ and $I[S_0(1)]$ are the integrated intensities of the $S_0(0)$ and $S_0(1)$ lines, ω_L is the laser frequency, and ω_0 and ω_1 are the frequencies of the $S_0(0)$ and $S_0(1)$ rotational lines, respectively. After a few hours of conversion our sample reached the equilibrium concentration $x_p=0.996\pm0.003$ as measured by means of Eq. (13), which compares very well with the theoretical value of $x_p(\mathrm{theor})=0.9961$ at $T=22$ K. Starting from this almost pure parahydrogen liquid sample we then created the crystal using the following procedure. We slowly cooled the sample from $T=22$ K to $T=18$ K with a rate of cooling of 1 K in 15 min, maintaining the laser light passing through the scattering cell with a constant power of 0.5 W during the crystal growth. The final thermodynamic conditions after the crystal growth are $T=18\pm0.5$ K and $p=244\pm0.5$ bars. Under these conditions we were able to grow a clear transparent crystal of parahydrogen with the c axis within a good approximation parallel to the laser-beam direction. This is presumably due to the small temperature gradient caused in the system by the laser beam itself along the direction of propagation of the light. We have verified the direction of the c axis of the single crystal which is grown in the scattering region by measuring the ratio of the total intensity of the one-phonon line at 44 cm^{-1} to the total intensity of the $S_0(0)$ rotational line as described in Ref. 8.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

We have measured the Raman spectrum of the fundamental band of a single crystal of parahydrogen at three slightly different temperatures and densities which are listed in Table I. The scattering geometry is the vertical one, in which the incoming beam is along the z axis and polarized along the x axis while the scattered light is detected along the y axis, summing both scattered polarizations I^{xx} and I^{xz}.

Figure 1 shows the scattering spectrum of parahydrogen at $T=18.5$ around the $Q_1(0)$ and $S_1(0)$ vibrational and rotovibrational transitions where the $S_1(0)$ part has been displayed with a factor-of-10 amplification. At the side of the $S_1(0)$ transition in the region around 4500 cm^{-1}, the $Q_1(0)+S_0(0)$ double transition band is clearly visible. Next to the main $Q_1(0)$ peak at 4149.4±0.2 cm^{-1} there is a weaker one at 4146.4±0.2 cm^{-1} due to the $Q_1(1)$ transition in the small fraction of ortho molecules present in the crystal. Figure 2 shows the spectrum of Fig. 1 around the $S_1(0)$ transition amplified by a factor of 20 in order to show the details of this part of the spectrum. From this figure it is clear that the $S_1(0)$ appears as a triplet with frequencies in cm^{-1} of 4482.4±0.2, 4485.2±0.2, and 4487.0±0.2, together with a well-structured $Q_1(0)+S_0(0)$ band. This is the first time that the triplet structure of the $S_1(0)$ Raman line and the appearance of the $Q_1(0)+S_0(0)$ double transition have been observed experimentally in H_2. In D_2 the double transitions have been observed previously, but the triplet structure was not resolved in that case.[1] Structure in the $S_1(0)$ of H_2 has also been observed in absorption[3] and discussed in the literature.[4,9] It is worth mentioning that the peak intensity of the $Q_1(0)+S_0(0)$ band is, in our apparatus, of the order of 1 photon/s. The double transition shows considerable structure which reflects that of the

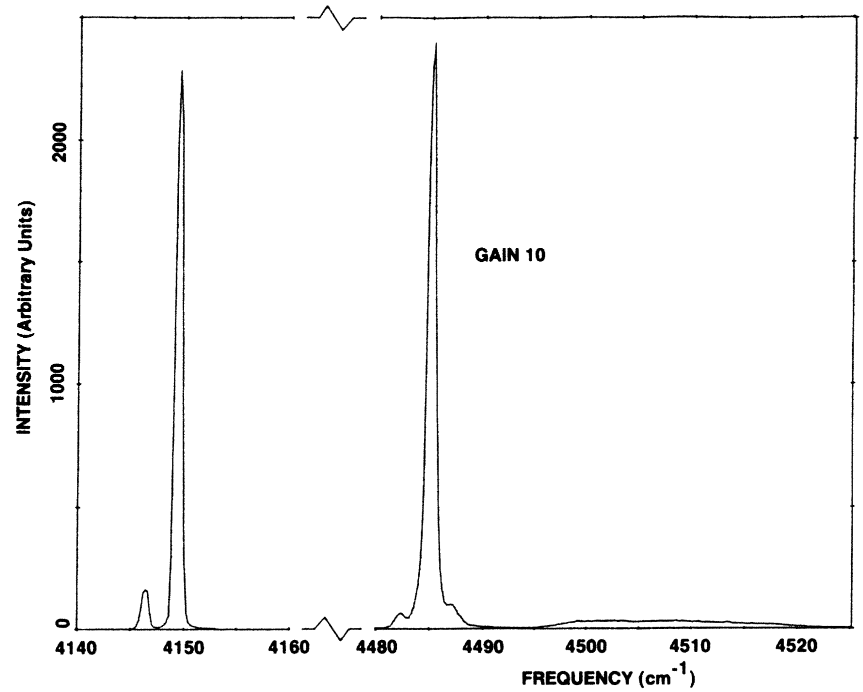

FIG. 1. Raman spectrum of parahydrogen at $T=18.5$ K around the $Q_1(0)$ and $S_1(0)$ transitions. The intensity around $S_1(0)$ is amplified by a factor of 10.

$Q_1(0)+S_1(0)$ manifold,[9] which is due to the effect of the EQQ interaction. This structure is also reflected in the double transition in absorption which has been known for a long time.[3] It should be stressed that the Raman double transitions are overwhelmingly associated with the allowed polarizability of the individual molecules, whereas the infrared absorption is due to the induced dipole operators in pairs of molecules. In order to establish that the intensity of the double transitions is due to the mixing of states, we compare experimental values of the ratio of double to single transitions with the theoretical expression given in Sec. II. The theoretical value of the ratio of double to single transitions as given in Eq. (12) involves the quantities λ and ξ_{54}. To calculate λ we use the quadrupolar matrix elements $\langle 00 | Q | 02 \rangle = 0.486ea_0^2$, $\langle 10 | Q | 12 \rangle = 0.537ea_0^2$,[10,11] which are known quite accurately; the energy separation of the unperturbed levels is $\Delta E = 18$ cm^{-1}. Using $R_0 = 3.79$ Å (Ref. 8) for the equilibrium separation at zero pressure we find the corresponding value of λ, viz. $\lambda_0 = 0.127$. For the parameter ξ_{54} a number of theoretical values, varying between 0.96 and 0.91, have been quoted.[5] Empirical values of 0.942 and 0.856 have been reported by Silvera[8] and by Hardy *et al.*,[12] respectively. Because our experiments are performed at relatively high temperature, the theoretical values for ξ_{54}, which are calculated at $T=0$, probably are not the correct ones to use. Using the two empirical values of ξ_{54} just quoted and $\lambda = \lambda_0 (R_0/R)^5$, where R is determined from the density of the samples given in Table I, and expression (12), we find the theoretical values for the ratio of double to single transitions given in Table I. It is seen that the value of $\xi_{54} = 0.856$ gives good agreement with experiment. Even if a higher value of ξ_{54},

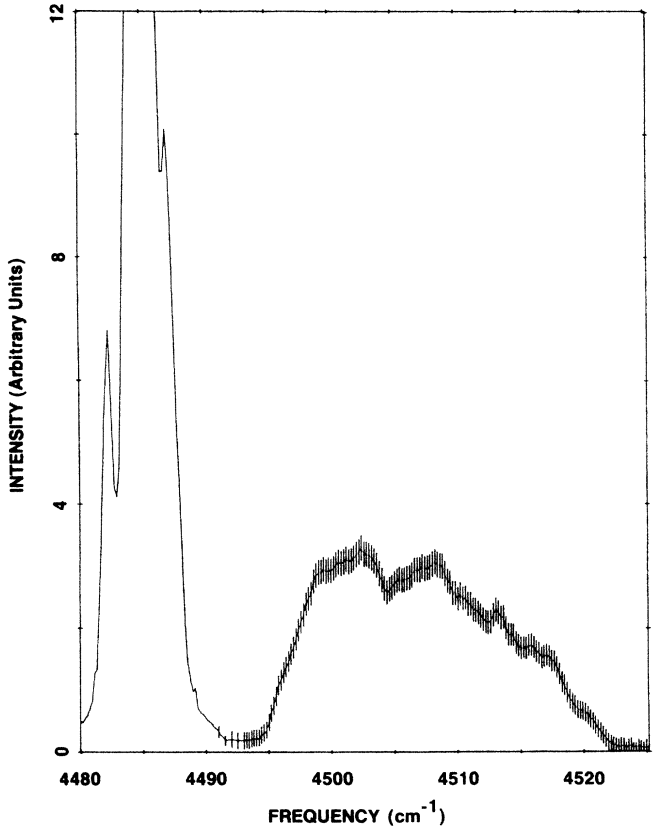

FIG. 2. Raman spectrum of parahydrogen at $T=18.5$ K around the $S_1(0)$ transition. The intensity is amplified by a factor of 20 with respect to Fig. 1. Error bars are shown for the double transition.

like the one given by Silvera, would be appropriate, the agreement between experiment and theory is close enough to establish our main point, viz. that the double transitions are predominantly due to the mixing of states as described above. If we actually fit ξ_{54} to our experimental results, we obtain a value of $\xi_{54}=0.83\pm0.04$. The present accuracy and range of densities is not adequate to test the predicted density dependence of the intensity ratio of $(\rho/\rho_0)^{10/3}$, which would be further confirmation of the assumed mechanism.

As an additional check on the reliability of the experimental results we have compared experimental and theoretical values for the intensity ratio of the sum of the $S_1(0)$ and $Q_1(0)+S_0(0)$ transitions to that of the $Q_1(0)$ transition. These experimental values, which depend crucially upon the spectral response calibration, because of the different polarization of the transitions compared, are also given in Table I. They agree to within experimental error with the theoretical value of 0.117 calculated from Eq. (3) for our scattering geometry, using $\langle 00 | \alpha | 10\rangle = 0.739a_0^3$, $\langle 00 | \gamma | 12\rangle = 0.571a_0^3$.[13] This agreement is also a test of the validity of spectroscopic stability in the case of the $S_1(0)$ and the $Q_1(0)+S_0(0)$ transitions.

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