

## Rapid Communication

# Direct Measurement of the Crystal Field Splitting of Isolated $J=1$ Impurities in Solid Parahydrogen

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The crystal field splitting of single  $J=1$  impurity orthohydrogen molecules in an otherwise pure  $J=0$  parahydrogen crystal has been studied experimentally and theoretically over many years. We have measured this quantity directly from the fine structure of the  $Q_3(0)$  ( $v = 3 \leftarrow 0$ ,  $J = 0 \leftarrow 0$ ) overtone transition induced by  $J=1$  hydrogen, in the near infrared using a Ti:sapphire laser. From our observed eight pairs of split spectral lines, we have determined the value  $\Delta/k = [E(M=\pm 1) - E(M=0)]/k = 0.0102 \pm 0.0003$  K including its sign. A straightforward numerical calculation based on *ab initio* calculations of the  $H_2$ - $H_2$  potential reported by Mulder, van der Avoird, and Wormer gives  $\Delta/k = 0.0116$  K which is close to the experimental value. This suggests that the static and dynamic effects of phonons on the splitting may have been overestimated in the past.

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An isolated  $J=1$  orthohydrogen "impurity" existing substitutionally in an otherwise pure  $J=0$  para- $H_2$  hexagonal close packed (hcp) crystal lattice is a clean system which has been studied extensively both theoretically and experimentally.<sup>1</sup> The introduction of this orthohydrogen molecule in place of parahydrogen yields a system which is nearly identical to the pure parahydrogen lattice. Dispersion is by far the dominant force binding the crystal and controlling intermolecular interactions, but the following three perturbative electric effects produce an isotropic excess binding energy and cause a homogeneous contraction of the lattice surrounding the  $J=1$   $H_2$ .

1. The average quadrupolar electric field of the  $J=1$   $H_2$  polarizes the

surrounding  $J=0$   $H_2$  leading to an excess binding energy of  $-\frac{3\alpha Q^2 S_8}{2R_o^8} \sim -1.12K$ , where  $\alpha$  and  $Q$  are the polarizability and the electric quadrupole moment of hydrogen, respectively,  $S_8 = 12.80$  is the lattice sum of  $(R_i/R_o)^8$ , and  $R_o$  is the intermolecular distance.

2. The second order electric quadrupole-quadrupole (EQQ) interaction between the  $J=1$   $H_2$  and the surrounding  $J=0$   $H_2$  leads to an excess binding energy of  $-\frac{7Q^4 S_{10}}{10BR_o^{10}} \sim -1.57 K$  where  $B = 59.23 \text{ cm}^{-1}$  is the rotational constant of  $H_2$ .
3. The increase of the internuclear distance in the  $J=1$   $H_2$  due to centrifugal distortion increases the polarizability by 0.18% leading to an excess dispersion energy of  $\sim -0.76 K$ .

There are other effects such as the variation of the repulsive potential for which *ab initio* calculations are needed and the dynamical effects of lattice vibrations for which phonon renormalization is needed.

In addition, anisotropic interactions are expected which depend on the orientation  $\Omega$  of the  $J=1$   $H_2$  in the form of the Racah spherical harmonics  $C_{20}(\Omega)$ . The effect of such terms is to split the sublevels of the  $J=1$   $H_2$  with different magnetic quantum numbers  $M$  that are degenerate in free space. The  $C_3$  symmetry of the hcp crystal keeps the two  $M=\pm 1$  levels degenerate but the  $M=\pm 1$  and  $M=0$  levels are split. It is this crystal field splitting, which we denote  $\Delta$ , that we address in this paper.

Schaefer<sup>2</sup> was the first to consider this splitting to explain the observed anomalous specific heat of solid hydrogen,<sup>3</sup> he obtained the value  $\Delta/k = 5.7 \pm 0.1 K$  It was shown by Nagamiya and Kisi,<sup>4</sup> however, that the splitting should be smaller because the anisotropic interaction between the  $J=1$  hydrogen and the crystal vanishes upon summation over the nearest and next nearest neighbors. Nakamura<sup>5</sup> introduced the EQQ interaction of the  $J=1$  hydrogen pair and explained a major portion of the anomaly. Using the remaining anomaly in the specific heat measurement for crystals with low orthohydrogen concentration,<sup>6</sup> he obtained the value of  $\Delta/k = 1.5 K$ .<sup>5</sup> Since then the specific heat measurement has tended to give high  $\Delta$  values as exemplified by  $\Delta/k = 0.87 K$  reported by Robert, Rojas, and Daunt.<sup>7</sup> In the mean time, theory gave values of  $\Delta/k = 0.52 K$ ,<sup>8</sup>  $1.9 K$ ,<sup>9</sup> and  $0.3 K$ .<sup>10</sup>

Since 1966, the value of  $\Delta$  has been found to be much lower through NMR experiments. From the linewidths of NMR signals, Harris and Hunt<sup>11</sup> deduced  $\Delta/k = 0.32 K$  and  $0.035 K$  for  $H_2$  and  $D_2$ , respectively. From the time dependence of the free induction decay, Hardy and Gaines<sup>12</sup> estimated  $\Delta/k = 0.0082 K$ . From a similar experiment using purer parahydrogen crystals, Constable and Gaines<sup>13</sup> obtained  $\Delta/k = 0.023 \pm 0.015 K$ . More recently

Schweizer, Washburn, and Meyer<sup>14</sup> obtained from the temperature dependent splitting of the  $J=1$  NMR doublet  $\Delta/k = 0.0083 \pm 0.002$  K. None of the experiments determined the sign of  $\Delta$  except that by Constable and Gaines<sup>13</sup> who concluded that the  $M=0$  level is higher in energy than are the  $M=\pm 1$  levels, a conclusion which turns out to be incorrect. The value of  $\Delta$  was also estimated from spectroscopic experiments which do not involve  $J=1$   $H_2$ . From the asymmetry of the triplet of the  $S_0(0)$  rotational Raman spectrum, Sears and van Kranendonk<sup>15</sup> estimated  $\Delta/k = 0.03 \pm 0.02$  K. If we use the value of  $V_c$  reported by Hardy, Harris, and Berlinsky<sup>16</sup> from their fine analysis of the  $J=1$   $H_2$  pair microwave spectrum, we estimate  $\Delta/k = 0.0142$  K. These estimates, however, are based on the assumption that the crystal field for the  $J=2$   $H_2$  or  $J=1$   $H_2$  pair is equal to that for the isolated  $J=1$  hydrogen molecule, which may not be correct in view of the different excess binding energies and thus different distortions of the lattice in each system. In the mean time, theoretical studies of Raich and Kanney<sup>17</sup> and Luryi and Van Kranendonk<sup>18</sup> gave  $\Delta/k = 0.0334$  K or  $0.0095$  K (depending on the assumptions used), and  $0.072$  K, respectively.

Overall we believe that it is fair to say that this important quantity  $\Delta$  has not been accurately determined. In this paper we report an experimental value of  $\Delta$  with an accuracy of 3% including its proper sign.

We observed the crystal field splitting of the  $J=1$  sublevels directly as splittings of the fine structure of the infrared  $Q_3(0)$  second overtone transition ( $v=3 \leftarrow 0$ ,  $J=0 \leftarrow 0$ ) at  $11758$   $cm^{-1}$ , in parahydrogen crystals containing approximately 0.1% orthohydrogen using a Ti:sapphire laser. The transition is caused by the dipole moments induced in  $J=0$   $H_2$  due to the quadrupolar electric field of the  $J=1$   $H_2$ . Since the quadrupolar field is angularly dependent, the  $J=1$  molecule also makes a simultaneous orientational transition,  $J=1, M' \leftarrow J=1, M$ , thus producing the fine structure. Observation of such fine structure in high resolution is not possible for the fundamental  $Q_1(0)$  transition because fast vibron hoppings among  $J=0$  molecules broaden the lines. The vibron hopping in the first overtone  $Q_2(0)$  transition slows enough to observe some of these transitions, but many are still overlapped, and therefore obscured.<sup>19</sup> For the  $Q_3(0)$  transition, the vibron hopping is reduced to the order of magnitude of 10 MHz and the splitting in the ground state of 213 MHz is readily resolved using high resolution laser spectroscopy. Observation of such sharp vibration-rotation spectra in nearly pure parahydrogen crystals has been recently developed in our laboratory.<sup>21,22</sup> Experimental details will be published in a separate paper.<sup>23</sup>

An overall spectrum observed in a sample containing 0.095% orthohydrogen at 4.2 K is shown in Figure 1 with iodine reference lines simultane-

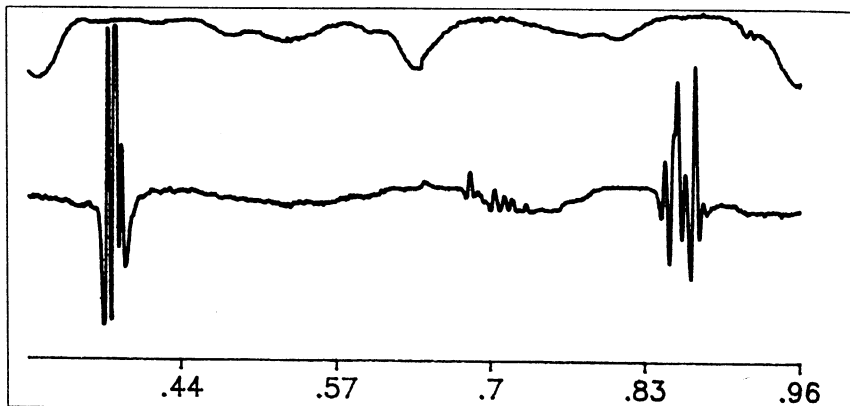


Fig. 1. The lower trace is the entire  $Q_3(0)$  absorption spectrum collected with toneburst modulation (50 MHz sidebands (tone) amplitude modulated at 30 kHz (burst), see ref. 28) for the laser polarization parallel to the crystalline axis yielding a second derivative lineshape. The zero of the x-axis corresponds to  $11758.000 \text{ cm}^{-1}$ . The upper trace gives iodine reference lines at  $11758.3222 \text{ cm}^{-1}$ ,  $11758.6374 \text{ cm}^{-1}$ , and  $11758.9660 \text{ cm}^{-1}$ . The transition frequencies were determined both from a wavelength meter with absolute accuracy of 220 MHz and from the iodine reference transitions.

ously recorded in the upper trace for frequency calibration.<sup>20</sup> Our samples are grown by depositing hydrogen gas on the walls of a copper cell such that the crystal growing temperature is approximately 7.25 K. Since solid parahydrogen contracts only slightly between 7.25 K and 4.2 K, the samples grown by this method are optically transparent and relatively free of cracks. Since our sample cell is cylindrical, the crystalline c-axis is consistently directed radially inward as we have shown spectroscopically in our analyses of many transitions.<sup>21</sup> Observations in different crystals yield identical values of  $\Delta$  to within the uncertainty in frequency measurement afforded by the laser scan linearity and published iodine reference frequencies. The fact that these samples are relatively free of inhomogeneous broadening due to strain or crystal defects is demonstrated by the narrowness of the  $Q_1(0)$  stimulated Raman transition (laser limited modulated linewidth of 7 MHz hwhm).<sup>24</sup> Three main sets of features are observed; the stronger sets separated by nearly  $0.5 \text{ cm}^{-1}$  arise from nearest neighbor pairs of  $J=1 \text{ H}_2$  and  $J=0 \text{ H}_2$ , while the weaker set near the center is due to next nearest neighbor pairs. The large splitting of  $0.5 \text{ cm}^{-1}$  corresponds to that of the  $J=1 \text{ H}_2$  next to the vibrationally excited  $J=0 \text{ H}_2$ ; the vibrational excitation breaks the  $D_{3h}$  symmetry of the crystal and the splitting is greatly enhanced since

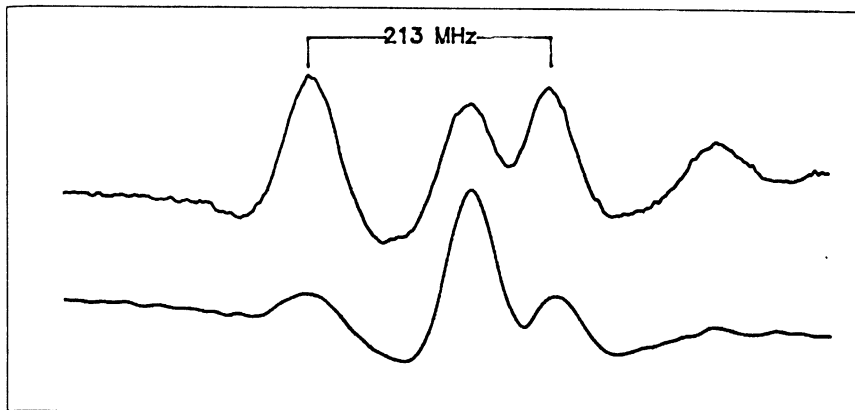


Fig. 2. Expansion of the low frequency set of transitions for both parallel (upper) and perpendicular (lower) polarizations. The first and third lowest frequency transitions are due to out of plane nearest neighbor  $J=1/J=0$  hydrogen molecules while the second and fourth are due to in plane neighbors. The splittings for each pair type is the crystal field splitting of an isolated  $J=1$  molecule ( $0.0071 \pm 0.0002 \text{ cm}^{-1}$  or  $0.0102 \pm 0.0003 \text{ K}$ ) and illustrates that the  $M=0$  state has lower energy than does  $M=\pm 1$ . The energies are determined from the centers of the second derivative line shape.

the lattice sum for nearest neighbors no longer vanishes (the polarizability of  $H_2$  increases by 36.5% upon the vibrational excitation<sup>25</sup>). The breakdown of symmetry also removes the degeneracy of the  $M=\pm 1$  levels; this together with the slight difference in energy for in plane and out of plane pairs leads to the intricate structure of each set. Using theoretically calculated intensity dependences on the polarization of the laser radiation, we have unambiguously assigned all 17 of the observed features.<sup>23</sup>

The small  $J=1$   $H_2$  splitting without vibrational excitation for  $J=0$   $H_2$  is shown in Figure 2 where the set of transitions near  $11758.39 \text{ cm}^{-1}$  is given with an expanded frequency scale for the polarization of the laser radiation both parallel and perpendicular to the crystalline  $c$  axis. Altogether eight such pairs of transitions are observed and led to the value  $\Delta/hc = 0.0071 \pm 0.0002 \text{ cm}^{-1}$  or  $\Delta/k = 0.0102 \pm 0.0003 \text{ K}$  and to the observation that the  $M=\pm 1$  levels are higher in energy than is the  $M=0$  level. This value agrees with the results of Schweizer, *et al.*,<sup>14</sup> within their quoted uncertainty and, perhaps fortuitously, is close to the second theoretical estimate of Raich and Kanney<sup>17</sup> although their theoretical methods have been criticized by Luryi and Van Kranendonk.<sup>18</sup>

Since the three electrostatic effects discussed at the beginning of this

paper give a very small value of  $\Delta/k = 0.0004$  K, the splitting has been often ascribed to uniform distortion of the crystal which leads to a deviation of  $c/a$  from  $(8/3)^{1/2}$  and to the dynamic effect of crystal oscillation.<sup>1</sup> If we employ the *ab initio* calculations of the anisotropic dispersion and induction interactions by Mulder, van der Avoird, and Wormer<sup>26</sup> without considering any lattice distortion, however, we obtain the value of  $\Delta/k = 0.0116$  K, which is close to our experimental value. Along with the previous results where such calculation gave a value of the  $J=6$  crystal field splitting close to the observed value,<sup>27</sup> we may conclude that the effect of phonon renormalization has been overestimated and that the anisotropic dispersion interaction with a small perturbation from induction yields an accurate crystal field splitting in contrast to published reports.<sup>1</sup>

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