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Research Article

On the Exothermic Response Frequencies When PdD Is Subjected to coherent THz Radiation

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Abstract

In this paper we identify the three specific frequencies in the $3-25$ THz range that have been found to trigger anomalous exothermy in PdD with low-lying dipole transitions in the spectrum of a single deuteron trapped at the octahedral site. We speculate that the state phase coherence that characterizes the ground state of the TavisCummings Hamiltonian may give rise to an increase in the rate of deuteron-deuteron fusion over that of stochastic deuterons.
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1. Introduction

In a series of really quite remarkable experiments, Letts and Hagelstein [1] succeeded in triggering an anomalous exothermy in ($PdD_{0.9}$) by means of laser radiation tuned to three specific infra-red frequencies in the range 3–24 THz. The frequency selectivity (Q-value) of the anomalies were in the range of 14–39, suggesting a lightly damped and narrow-band resonance response of the target material. Hagelstein has put forward an explanations for the exothermy based on the fact that the two lower response frequencies correspond to points of zero group velocity in the optical phonon bands, but he has been unable to account for the other (stronger) response at 21 THz. We however question his phonon-band interpretation because zero group velocity implies zero propagation of energy along the chain of oscillators. Indeed we question whether it is even possible to speak of phonon bands when a significant percentage of the sites are vacant.

We are unaware of any other credible attempts to explain this remarkable phenomenon and attribute this to a general scepticism regarding the calorimetric data that we certainly do not share. In this paper we draw attention to the fact that all of the observed exothermic response frequencies correspond to low-lying dipolar transitions in the vibration spectrum of individual noninteracting trapped deuterons. We then point out that when the laser radiation is of sufficient intensity, all of the deuterons will cohere in a long-lived Dicke ground state and that this would lead to an enhancement of the normally negligible deuteron-fusion rate by a factor equal to the number of deuteron neighbours.

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2. Laser-Deuteron Interaction Hamiltonian

We are going to make several simplifying assumptions. The first of these is that the laser radiation frequency ω excites transitions between a single pair of states in the deuteron vibrational spectrum (with $|E_i - E_j| = \hbar\omega$) and that the plane of polarization is along one of the fcc axes, which we will label x.

According to the Drude model [2], the complex refractive index of Pd at THz frequencies is given approximately by:

$$\epsilon = 1 - \frac{\omega_P^2}{\gamma^2 + \omega^2} + \frac{\omega_P^2 \gamma}{\omega\left(\gamma^2 + \omega^2\right)} i \tag{1}$$

implying

$$\sqrt{2}n = \sqrt{|\epsilon| + \mathrm{Re}\{\epsilon\}} + \sqrt{|\epsilon| - \mathrm{Re}\{\epsilon\}}\, i \tag{2}$$

Using $\hbar\omega_P = 2.77$ eV and $\hbar\gamma = 0.068$ eV as published in [3], n at 10 Thz $\approx 24 + 43i$. This means that the laser radiation only penetrates to a depth of around one micron.

Within this surface layer, we envisage N deuterons occupying an equal number of interstitial sites of octahedral symmetry. In other words, we assume stoichiometry and translational invariance.

An assembly of non-interacting two-state quasi atoms driven resonantly by a field of coherent radiation is most simply modelled by the Tavis-Cummings Hamiltonian in which the 2^N state space is transformed into that of a single quasi-spin multiplet. Following [4] and [5] we have

$$H_{TC} = \hbar\omega a^\dagger a + \hbar\omega\left[\frac{N}{2} + S_3\right] + g\left(a^\dagger S_+ + a S_-\right) \tag{3}$$

The sum of the number of photons and excited sites is a conserved quantity (N_{exc}) and the energy levels are given by

$$E_j = N_{exc}\hbar\omega + 2jg\sqrt{N_{exc}} \tag{4}$$

where $-N/2 \leq j \leq N/2$.

The lowest energy is clearly $E_{-N/2} = N_{\mathrm{exc}}\hbar\omega - Ng\sqrt{N_{\mathrm{exc}}}$ and the gap between levels is $\Delta E = g\sqrt{N_{\mathrm{exc}}}$ The field amplitude E_0 of a single photon over N sites each of volume Ω is given by

$$\hbar\omega = 2n^2\epsilon_0 E_0^2 N\Omega \tag{5}$$

where n is the real part of the refractive index at ω.

In a surface layer of depth $\lambda/2$, the coupling to the E-field will vary strongly with position, being greatest for sites at the centre of the layer, but the mean photon-site coupling is approximately described by

$$g_{ij}^2 = e^2 E_0^2 |< i|x|j >|^2 = \frac{e^2 |< i|x|j >|^2 \hbar\omega}{2Nn^2\Omega\epsilon_0} \tag{6}$$

3. Palladium Deuteride

Palladium is one of several transition metals that can reversibly absorb hydrogen up to the point of stoichiometry, in which every available interstitial site of octahedral (O) symmetry is occupied by a hydrogen nucleus. As pointed out above, the large mass ratio between the hydrogen nucleus and the host atoms, means that the quantum oscillation is decoupled from the motion of host atoms and the interstitial hydrogen nucleus (p, D) experiences an effective static potential, with local mimina at the octahedral and tetragonal symmetry points. Furthermore, each deuteron is screened

by the Fermi gas such that intersite deuteron-deuteron interactions are small. The screened deuterons are effectively almost neutral particles, resulting in high mobility within the lattice and a very shallow effective potential. As a consequence, even the ground state has a substantial spatial extent on the order of 0.2Å.

A single deuteron in such an environment exhibits a spectrum of singlet, doublet and triplet state representations of the local point symmetry group. The ground state is a singlet with even parity about the minimum potential along each of the symmetry axes. The next level is a triplet of states with odd parity along one of the symmetry axes and an excitation energy of the order of 0.04 eV($\approx$ 10 THz). The real and imaginary parts of the refractive index are comparable in this part of the spectrum, so there is effectively only one internally reflected mode along each of the x, y and z axes. and a single photon is effectively normalized to a slab volume $A\lambda/2$. We conclude that microlayers of non-stoichiometric PdD are amenable to the Tavis-Cummings model in which a single photon mode is coupled to N identical two-level quasi-atoms.

In PdD, each interstitial octahedral site corresponds to a volume $\Omega = \frac{1}{4}a^3 \approx 1.6 \times 10^{-29}$ m^3, so

$$\frac{e^2}{\epsilon_0 \Omega} \approx 1.1 \times 10^{21} \text{ eVm}^{-2} \tag{7}$$

and the dipole transition coupling coefficient is given by:

$$g_{ij}^2 \approx \frac{\hbar\omega_{ij}| < i|x|j > |^2}{Nn^2} \times 5.5 \times 10^{20} \text{ eVm}^{-2} \tag{8}$$

We chose the x axis as our dipole and E-field direction, but exactly the same results would be obtained for y and z axes by virtue of the fcc point symmetry at the octahedral site. μ_x dipoles can only be formed by products of states that have opposite x-parity and equal y and z parities.

We solved the $[.++]$ deuteron states on a 3-dimensional grid of pitch 0.25Å using the semi-empirical effective potential published in [6] and were able to substantially confirm the findings of that paper. We checked all dipoles of states involving $[.+-], [.-+], [.--]$, but none of these were larger than those involving $[.++]$ parity states and they lie at higher energies, so we do not consider them here.

The energy levels E_i (relative to the potential minimum at the octahedral symmetry point) of the ten lowest states in each of the $[+++]$ and $[-++]$ subgroups are listed below:

i, j	$E_{i_{[+++]}} \times 10^{-3}$ eV	$E_{j_{[-++]}} \times 10^{-3}$ eV
0	**47**	**88**
1	138	173
2	**190**	190
3	217	**213**
4	**148**	248
5	**148**	182
6	233	283
7	233	283
8	283	**277**
9	284	289

$[+++]$ states $\{4, 5\}$ and $\{6, 7\}$ are degenerate doublets. None of lowest $10[-++]$ states are degenerate The largest μ_x dipole elements are tabulated below, together with the dimensionless photon mode coupling constants $g_{ij}\sqrt{N}/(\hbar\omega)$:

$i_{[+++]}$	$j_{[+--]}$	$\lvert E_i - E_j \rvert \times 10^{-3}$ eV	= THz	E_{lower}	$\langle i\lvert x\rvert j\rangle$(Å)	$g_{ij}\sqrt{N}/(\hbar\omega)$
0	0	40	9.8	47	0.16	0.08
1	3	74	18.0	138	0.10	0.07
2	8	87	21.1	190	0.08	0.07
3	1	45	10.8	173	0.17	0.09
3	6	66	15.9	217	0.12	0.08
$4+5$	3	65	15.7	148	0.19	0.11
6	5	51	12.4	182	0.14	0.08
6	9	56	13.6	233	0.15	0.09
7	5	51	12.4	182	0.14	0.08
7	9	56	13.6	233	0.15	0.09
9	3	72	17.3	213	0.12	0.09

Because the $[+++]$ parity states 4 and 5 are degenerate, we have added their dipole products with $[-++]$ state 3 in quadrature.

3.1. Second Order Effects

It should be understood that the above tabulations are first-order in the photon-dipole interaction. This rotating wave approximation (RWA) does not allow for the effects of virtual processes that transiently change the n_{exc}. There will also be second order effects on the transition frequencies arising from mixing with states that are higher up the excitation ladder. Interstitial hydrogen nuclei have a complex vibrational spectrum. Any correlation with the actual empirical response frequencies is hence going to be approximate and subject to error bars that are extremely hard to quantify.

4. Tentative Identification of the Response Frequencies

The 0-0 transition corresponds to the Γ point of the optical phonon band.

Comparison with Fig 10b of [1] leads us to make the tentative identifications (shown in bold) of the three responses observed at $8.3, 15.1$ and 20.5 THz with the theoretical dipole transitions at $9.8, 15, 7$ and 21.1 THz. Our second tabulated entry also predicts a strong dipole transition at 18.0 Thz that is not visible in the fitted curve of Fig 10b of [1]. However the raw data in their Table 1 does indeed show an observed exothermic response at 18.0 Thz, which was evidently overlooked in the curve fitting.

We can not exclude the possibility that the numerical correspondence noted above is merely a coincidence and that the actual mechanism for frequency-selective exothermic response has nothing to do with dipole transitions.

5. The Coherent N-Deuteron State

Every eigenstate of (3) comprises contributions from every one of the 2^N states of the deuterons. In the absence of intersite interactions, the lowest singlet eigenstate is the simple product of N one-particle wavefunctions:

$$\Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_k \ldots\ldots \mathbf{r}_N\right) = \prod_{k=1}^{N} \left[c_i \psi_i\left(\mathbf{r}_k - \mathbf{R}_k\right) + c_j \psi_j\left(\mathbf{r}_k - \mathbf{R}_k\right)\right] \equiv \prod_{k=1}^{N} \psi_{ij}\left(\mathbf{r}_k - \mathbf{R}_k\right) \tag{9}$$

$$c_i^2 = \frac{1}{2} - \eta \text{ and } c_j^2 = \frac{1}{2} + \eta \quad \text{where } \lim_{N\to\infty} \eta(N) = 0 \tag{10}$$

The superposition mimics the classical response of charged monopoles oscillating about their equilibrium positions in synchronism with the applied oscillating E-field. The only other Tavis-Cummings state that is a simple product is

the highest. This state differs from the lowest state solely in regard to the sign of $\frac{c_j}{c_i}$. It corresponds to a vibration in counterphase to the E-field.

Realistically, the H_{TC} must be supplemented by an interaction potential $U(r)$ between neighbouring deuterons at sites with relative separation vectors $\mathbf{R}_k - \mathbf{R}_{k'} = \left\{0, \pm\frac{a}{2}, \pm\frac{a}{2}\right\}$ *et cycl.* This interaction is a modified Weidel-ThomasFermi potential for separations greater than the nuclear radius and an imaginary optical potential for subnuclear separation, as shown in Fig. 4 of [7]:

$$U(r) \approx \frac{e^2}{4\pi\epsilon_0 r} e^{-\kappa r} \cos \kappa r \text{ for } r > r_{\text{deut}} \tag{11}$$

$$U(r) = iW(r) \text{ for } r \leq r_{\text{deut}} \tag{12}$$

$U\left(\frac{a}{\sqrt{2}}\right) \approx 0.005$ eV so there is a small first-order energy shift (upwards) per site. The second-order modification of the pair wavefunction is negligible at the intersite separation. We can represent the perturbation in terms of an anti-correlation (attenuation) function $\phi(r)$ that is 1 at $r = a/2$ and which falls exponentially at $r \ll a$ as a result of the repulsive Coulomb interaction:

$$\psi_{ij}\left(\mathbf{r}_1, \mathbf{r}_2\right) = \psi_{ij}\left(\mathbf{r}_1 - \mathbf{R}_k\right) \psi_{ij}\left(\mathbf{r}_2 - \mathbf{R}_{k'}\right)) \, \phi\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \tag{13}$$

For each pair of neighbours, the fusion rate is proportional to

$$\int d^3\mathbf{r}_1 \int_{|\mathbf{r}_1 - \mathbf{r}_2| < r_{\text{deut}}} \psi_{ij}^{\dagger}\left(\mathbf{r}_1, \mathbf{r}_2\right) W \psi_{ij}\left(\mathbf{r}_1, \mathbf{r}_2\right) d^3\mathbf{r}_2 \tag{14}$$

As is well-known and understood, this rate is vanishingly small because $U\left(r_{\text{deut}}\right)$ is on the order of 100 KeV.

The energy gap to the next lowest level (an N-tuplet) of the (interaction modified) H_{TC} is $\sqrt{N_{exc}/2}g\hbar\omega$. In the experiments [1], N_{exc} was an unknown quantity because the THz radiation was produced from nonlinear mixing of the light from two red lasers and the efficiency of that mixing has not yet been ascertained. However we conclude from (4) that if the laser radiation is sufficiently strong, the thermodynamically favoured state of the N deuterons is one in which they occupy the lowest energy state described above, for times much longer than the vibrational period.

6. Further Work

State coherence per se should not have any effect on the fusion rate. However, if we consider the time-dependent Hamiltonian for two neighbouring deuterons in the coherent E-field, the transverse dipole-dipole interaction, which is intrinsically very small, is magnified by a factor $\sqrt{N_{\text{exc}}}$. This will lead to an effective attractive potential that at least partially cancels the Coulomb repulsion. I am currently working on an explicit calculation of this.

Fusion events arising out of this mechanism will be intrinsically delocalised over the coherence volume. No high energy fusion product, such as gamma rays, can emerge from such a volume on account of their tiny wavelength relative to the region of phase coherence. We conclude that the 24 MeV excitation will relax via a large number of low energy quanta, such as phonon excitations.

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