

Condon Modulation Spectroscopy of Solid Hydrogen and Measurement of the Temperature Dependence of the $Q_1(0)$ Transition

Karen E. Kerr, Takamasa Momose, David P. Weliky, Charles M. Gabrys, and Takeshi Oka

Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

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The Condon effect, in which an electric field induces otherwise forbidden transitions, has been used for inducing and modulating the $Q_1(0)$ vibrational infrared spectrum in para- H_2 crystals. The field induced spectrum obeys the exciton momentum rule, $\Delta\mathbf{k}=0$, and is very sharp. The modulation method has greatly improved the sensitivity and simplified the experiment. The method has been applied to study the temperature dependent frequency shift and broadening of the spectral line. The observed frequency shift has been explained as due to variations of matrix shift and vibron hopping frequency.

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In recent years, the study of intermolecular interactions in solid hydrogen has been greatly facilitated by the use of modern high resolution spectroscopic techniques [1,2]. While spectral lines with resolutions of $\Delta\nu/\nu \sim 2 \times 10^{-8}$ have been observed in this system, the sensitivity of the spectroscopy remained limited to $\Delta I/I \sim 2 \times 10^{-4}$ by the lack of suitable molecular modulation techniques. In this Letter, we report our use of the Condon effect [3] for modulation to enhance the sensitivity of solid hydrogen spectroscopy by 2 orders of magnitude. We have applied this technique to the study of the temperature dependence of intermolecular interactions involved in exciton band formation and of relaxation processes associated with the $Q_1(0)$ ($\nu=1 \leftarrow 0, J=0 \leftarrow 0$) transition.

Stark modulation and phase sensitive detection have become commonplace in spectroscopy since its initial introduction to the microwave region by Hughes and Wilson [4]. It is widely used in the spectroscopy of gasses, and, more recently, in solids [5-7]. While Stark modulation, which exploits the shift in frequency of spectral lines in the presence of an electric field, has brought orders of magnitude improvement in sensitivity, this effect is too small to be effectively used in solid hydrogen.

As initially pointed out by Condon [3], an electric field also *induces* otherwise forbidden infrared transitions in homonuclear diatomic molecules which obey Raman selection rules. Such transitions, which appear at the frequencies of the corresponding Raman transitions, were first observed in hydrogen by Crawford and Dagg [8]. The effect has been used by many others for spectroscopic studies of pressurized gaseous hydrogen [9] and nitrogen [10] and for studies of diamond [11]. Intensity modulation of the induced signal was first used by Terhune and Peters [12] for pressurized gaseous hydrogen and more recently by Colvin and Alivisatos for CdSe nanocrystals [13].

The Condon effect appears in its purest form in the $Q_1(0)$ transition of para- H_2 crystals. Unlike in pressurized gasses and in other solids in which the transition is already allowed by other interactions, the field induced transition in para- H_2 crystal is background free apart

from the broad and weak transition induced by ortho- H_2 impurities [14]. Furthermore, the Raman selection rules, which the induced transition obeys, hold not only for the molecular quantum number J but also for the exciton momentum, $\Delta\mathbf{k}=0$. Only the $\mathbf{k}^+=0$ level in the $Q_1(0)$ vibron band is active and therefore the transition is extremely sharp (~ 50 MHz HWHM). The sharpness of the spectrum with its intensity and purity allows us to study molecular interactions in solids through the observation of the temperature dependencies of the line position and linewidth.

The cryostat used in this work is similar to that employed for other infrared studies from this laboratory [1,2]. A flat surface which serves as the ground electrode for the homogeneous electric field was formed by partially filling the cylindrical cell with solid copper. The Stark electrode is formed from a circular copper plate (8 mm diameter, 2 mm thick) and is positioned 5 mm from the ground electrode. The cell is mounted on the temperature controlled stage of an Infrared Laboratories HD-3(8)L liquid helium Dewar. To ensure that the area between the electrode is filled with solid hydrogen, it is imperative that the Stark electrode be heat sunk directly to the helium can. We used a thermally conductive, but electrically insulating epoxy for this purpose. Para-enriched gas (99.8% p - H_2) prepared in the usual manner [1,2] is made to flow into the cell at such a rate as to maintain a stage temperature of ~ 7 K. When the volume of the cell has been filled, the sample is allowed to cool to 4.9 K. Radiative heating through openings in the heat shield prevented cooling to 4.2 K.

Tunable infrared radiation from a difference frequency system or a color center laser with spectral purities of ~ 10 and 3 MHz, respectively, was used for the spectroscopy. The maximum electric field that could be applied before breakdown occurred depended upon the sample. The discharge usually occurred near the high voltage feedthrough into the cell, rather than between the electrodes. Fields of 4-8 kV/cm were typically used in these experiments.

The field induced $Q_1(0)$ transition observed by using a

difference frequency system is shown in Fig. 1. Figure 1(a) shows a spectral line induced by a dc electric field of 8 kV/cm recorded using amplitude modulation of the infrared radiation with a chopper. Figure 1(b) shows the same spectral line recorded using Condon modulation with a 10 kHz ac field of 6 kV/cm peak to peak and $2f$ phase sensitive detection. From the observed signal to noise ratio and absolute intensity, the sensitivity of the spectroscopy is estimated to be $\Delta I/I \sim 5 \times 10^{-6}$. The frequency of the spectral line, measured from a CH₄ reference line [15] to be $4149.6918 \text{ cm}^{-1}$, agrees well with that of the previously reported stimulated Raman gain spectrum of the $Q_1(0)$ transition [16]. The width of the spectral line in Fig. 1 is measured to be 65 MHz HWHM. The line position and the linewidth are sharp functions of the impurity concentration [14] and crystal stress and varied greatly depending on the crystals. The line position varied as much as 0.03 cm^{-1} for different crystals. For a given crystal, the line position varied up to 0.003 cm^{-1} after several days of experimentation. This is possibly due to annealing of the crystal and/or rotational-diffusion of the ortho-H₂ impurities.

The integrated intensity of the field induced $Q_1(0)$ transition for parallel dc and laser electric field is obtained from Condon's theory using the relationship

$$\int \gamma(\nu) d\nu = \frac{8\pi^3 \nu}{3hc} n(a_{01}E)^2, \quad (1)$$

where $\gamma(\nu)$ is the absorption coefficient in cm^{-1} , n ($2.61 \times 10^{22} \text{ cm}^{-3}$) [17,18] is the number density of H₂ in the crystal, and a_{01} ($0.170 \times 10^{-24} \text{ cm}^3$) [19] is the off-diagonal matrix element of the isotropic polarizability. For a typical field of $E = 4.8 \text{ kV/cm}$, we calculate a transition moment of $2.7 \times 10^{-6} \text{ D}$ and a peak absorption of $\sim 10\%$ for a linewidth $\sim 50 \text{ MHz}$ HWHM which agrees approximately with the observed absorption. The Stark shift of the spectral line is calculated from the formula $\Delta\nu = -\Delta\alpha E^2/2h$ (where $\Delta\alpha = 0.070 \text{ \AA}^3$ is the difference of polarizability between the excited and the ground vibrational states) [19] to be -1.3 kHz which is negligible compared with the linewidth.

The use of Condon modulation not only enhances the sensitivity of the spectroscopy by 2 orders of magnitude but also greatly simplifies Raman type spectroscopy of the $Q_1(0)$ transition. The experimental setup is much simpler than that for a stimulated Raman experiment [16]. Furthermore, the laser power needed for the spectroscopy is considerably less, thereby making the crystal more durable. This allowed us to measure the temperature dependence of the line position and the linewidth accurately.

Several examples of the observed spectral lines at different temperatures are shown in Fig. 2. As the temperature is raised from 4.9 to 13.5 K, just below the triple point, the line position shifts to the blue by 4.2 GHz and the linewidth increases by a factor of ~ 3 . The line positions and the linewidths are reproducible for different

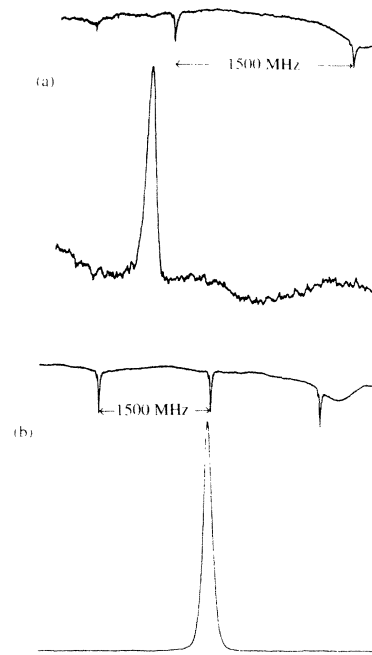


FIG. 1. Observed field induced $Q_1(0)$ ($\nu = 1 \leftarrow 0$, $J = 0 \leftarrow 0$) transition in 99.8% pure para-H₂. The sharpness of the spectrum is due to the long relaxation time of the rovibrational quantum states and the vibron momentum selection rule $\Delta k = 0$. A difference frequency system was used as the radiation source. The wave number of the spectral line was measured to be $4149.6918 \text{ cm}^{-1}$ using a CH₄ reference line at $4149.6325 \text{ cm}^{-1}$ (shown by arrows), and the linewidth $\sim 65 \text{ MHz}$ HWHM using the interference markers. In (a), a dc electric field of 8 kV/cm was applied and video detection using a chopper was employed. In (b), Condon modulation with a 10 kHz sine wave ac field of 6 kV/cm peak to peak was used followed by $2f$ phase sensitive detection. A sensitivity of $\Delta I/I \sim 5 \times 10^{-6}$ was obtained for a time constant of 3 sec. The laser polarization is parallel to the applied field. The signal disappears when they are perpendicular.

temperature cycles and the integrated intensity remains approximately constant.

The observed temperature dependence of the line position is plotted in Fig. 3. It fits well by an empirical formula

$$\delta\nu = 8.893 \times 10^{-2} T^{4.096} \text{ MHz}, \quad (2)$$

which is shown by the solid curve in Fig. 2. The similarity of this power law with that of the molar volume [$\delta V(T) = 2.233 \times 10^{-6} T^{4.424} \text{ cm}^3/\text{mol}$] [20] strongly suggests that the temperature shift can be explained simply in terms of the temperature variation of the intermolecular distance. We consider here two effects, the matrix shift of the vibrational frequency $\Delta\nu(T)$ and the hopping rate $\epsilon'(T)/2$ of the vibrational excitation (vibron) [14]. The line position $\nu(T)$ can be expressed as

$$\nu(T) = \nu_{\text{gas}} - \Delta\nu(T) - S_6 \epsilon'(T)/2, \quad (3)$$

where ν_{gas} is the vibrational frequency of free H₂. The

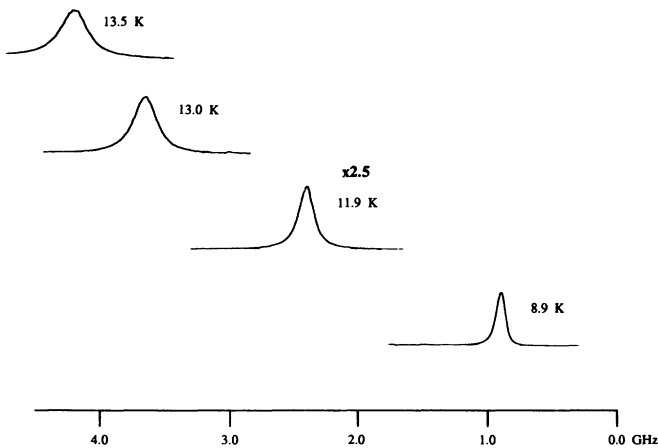


FIG. 2. Observed temperature shift and broadening of the $Q_1(0)$ spectral line. As the temperature is raised from 4.9 to 13.5 K, the line is blueshifted by ~ 4 GHz and broadens by a factor of ~ 3 . The line shape changes from a more Gaussian shape at low temperature to a Lorentzian shape at high temperature. The lines for the three higher temperatures are magnified by 2.5 for clarity. The integrated intensity remains the same. The line shifts and broadening are reproducible for temperature cycles for the same crystal.

last term of Eq. (3) represents the shift of the Raman activity $\mathbf{k}^+ = 0$ vibron Bloch state [14], in which S_6 is the lattice sum $\sum_i (R_0/R_i)^6$ and has the value of 14.455. Since the dispersion force is thought to be the dominant interaction for both matrix shift and vibron hopping, we assume that $\Delta\nu(T)$ and $\epsilon'(T)$ vary as R^{-6} . We then expect their variation to be proportional to $-6dR/R$ or $-2dV/V$. Using the gaseous value [21] $\nu_{\text{gas}} = 4161.81 \text{ cm}^{-1}$, we find the temperature variation of the line shift to be

$$\begin{aligned} \delta\nu(T) &= \nu(T) - \nu(0) = 2(\nu_{\text{gas}} - \nu_0)\delta V(T)/V \\ &= 6.68 \times 10^{-2} T^{4.424} \text{ MHz}, \end{aligned} \quad (4)$$

where $\delta V(T)$ given earlier and $V = 23.06 \text{ cm}^3/\text{mol}$ are used [18]. The observed shift of Eq. (2) is 9% lower than this value, at $T = 13.5 \text{ K}$.

Spectral shifts due to temperature variation were reported earlier by Jochemsen, Statt, and Hardy [21] in their microwave spectrum of ortho- H_2 pairs. They observed *redshifts* ranging between -1.65 and -12 MHz for five different pair transitions when the temperature was varied from 1.2 to 4.2 K. The redshifts were also explained by the temperature variation of the intermolecular distance which changed the pair splittings via the $1/R^5$ dependence of the dominant electric quadrupole interaction. Their observed values were 2 to 3 times larger than the calculated values. A similar analysis based on the R^{-6} dispersion interaction was given by Silvera, Jeon, and Lorenzana [22] to explain the difference between the pressure shifts of infrared and Raman vibron spectra.

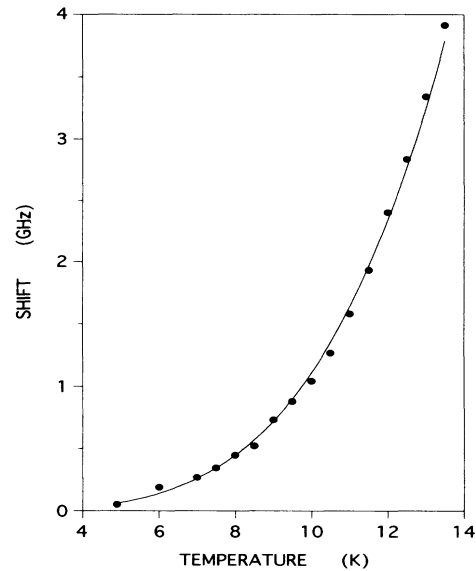


FIG. 3. Observed temperature shift of the frequency. The solid line shows the curve $\delta\nu(T) = 8.893 \times 10^{-2} T^{4.096} \text{ MHz}$, which was obtained by least squares fit of the observed $\delta\nu$.

We found that the linewidths depended more on individual crystals than did the frequency shifts. An example of the measurements is shown in Fig. 4. In general the linewidth increases only slightly between 4.9 and 10 K and much more drastically above 10 K. Some temperature independent effects such as the inhomogeneous broadening due to ortho- H_2 and deuterium impurities dominates at low temperature, and temperature dependent uncertainty effects due to phase and population relaxation take over at higher temperature. This interpretation is consistent with the observed variation of the line

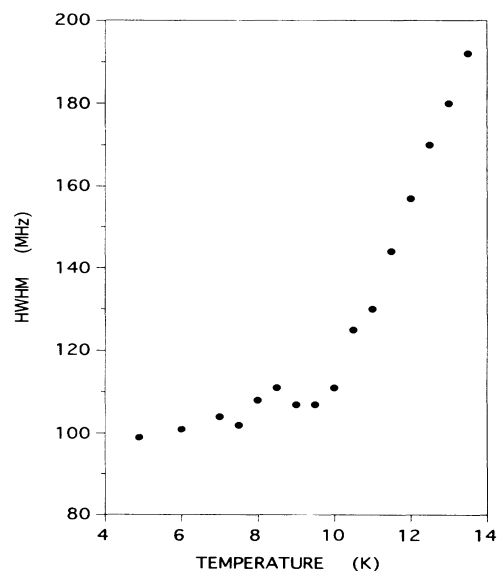


FIG. 4. Observed temperature dependence of the linewidths.

shape from more Gaussian profiles at low temperature to almost perfect Lorentzian profiles at high temperature. When the observed linewidths are fit by a temperature dependent Voigt profile, we obtain inhomogeneous linewidths of 50–100 MHz (HWHM) and homogeneous linewidths which depend on temperature as T^4 – T^9 depending on the crystal.

The physical effects that give rise to the linewidths and their temperature variation are not well understood. The inhomogeneous broadening results from level shifts and the violation of the vibron momentum rule $\Delta\mathbf{k}=0$ due to impurities. The homogeneous linewidth due to populational relaxation $(2\pi T_1)^{-1}$ seems to be very small (~ 0.1 MHz) in view of the long T_1 values reported for the $Q_1(1)$ transition [23,24]. The linewidth due to decay of coherence $(2\pi T_2)^{-1}$ is larger as read from the time resolved Raman study of the $Q_1(0)$ transition by Abram *et al.* [25]. Obviously more theoretical work [26,27] is needed to understand the linewidth and its temperature variation.

In summary, the method of Condon modulation has greatly enhanced the sensitivity and efficiency of solid hydrogen spectroscopy. The temperature dependence of the field induced $Q_1(0)$ transition has provided additional insight into the intermolecular interactions in vibron band formation and relaxation. This method will be applied to a wide variety of measurements in the spectroscopy of solid hydrogen and impurities.

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