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Pressure Dependent Vibrational Fermi Resonance in Liquid CH_3OH and CH_2Cl_2

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The vibrational Fermi resonance of two liquids, methanol (CH_3OH) and dichloromethane (CH_2Cl_2), is investigated by measuring changes in the position and intensity of Fermi-coupled Raman bands as a function of pressure, in a diamond anvil cell. The Fermi resonance of interest occurs in the 2900 cm^{-1} spectral region, where coupling between the CH symmetric stretch fundamental and a CH bend overtone gives rise to two prominent bands. The methanol results reveal a pressure induced transition through exact resonance at 1.25 GPa, where the two coupled states decompose into a pair of fully mixed hybrid bands. In dichloromethane, on the other hand, the two coupled states are driven farther apart and become less mixed with increasing pressure. The Fermi resonance coupling coefficient, W, is found to be constant in each liquid up to pressures exceeding 1 GPa ($W \approx 52.6$ and 22.3 cm^{-1} in CH_3OH and CH_2Cl_2, respectively). The anharmonic shift of the CH bend is about 10 cm^{-1} in both liquids, determined by comparing the frequencies of the fundamental and Fermi resonance corrected overtone. The results are compared with those of previous Fermi resonance studies using solvent, phase, isotope, temperature, and pressure variation. In addition to yielding a robust method for quantifying Fermi resonance, pressure variation is shown to offer a powerful aid to the resolution of spectral assignment ambiguities.

I. Introduction

The phenomenon of Fermi resonance arises from the mixing of vibrational modes of similar energy and symmetry (as the result of anharmonic coupling).[1] A classic example found in many organic compounds is the strong Fermi resonance typically observed between nearly resonant CH stretch fundamentals and CH bending overtones.[2] The associated wave function mixing produces readily measurable frequency shifts and intensity changes in the vibrational spectrum. Thus a normally forbidden vibrational transition (such as the CH bend overtone) may appear as a prominent peak in an infrared or Raman spectrum, at an observed frequency that is shifted away, or “repelled”, from its Fermi-coupled sister band.

In this work, pressure-induced changes in Raman spectra of liquid methanol (CH_3OH) and dicholoromethane (CH_2Cl_2) are used to quantify intramolecular Fermi resonance perturbations and anharmonic shifts in these two substituted methane molecules, using a simplified two-state model for the Fermi coupling. In particular, pressure dependent changes in the observed frequency splitting, δ, and intensity ratio, R, of bands arising from the CH stretch fundamental and CH bend overtone are used to determine the associated Fermi resonance coupling coefficient, W, unperturbed peak separation, δ_0, and the anharmonic shift of the CH bend, x. The results also illustrate the utility of pressure dependent Fermi resonance studies in resolving ambiguous assignments in polyatomic vibrational spectra.[3,4]

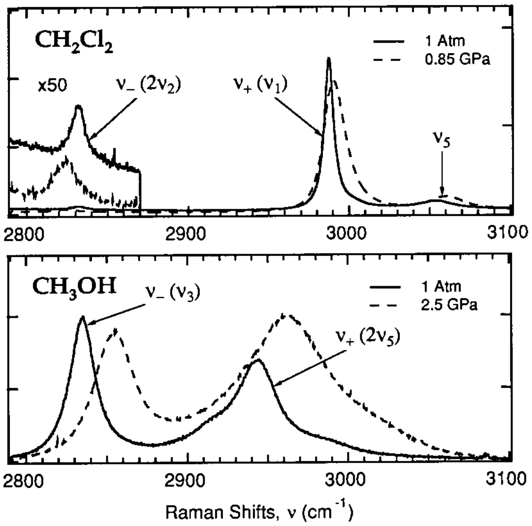

Figure 1. Raman spectra of Fermi resonant modes in the CH stretch region of liquid CH_2Cl_2 and CH_3OH, at different pressures.

The liquids chosen for this study represent two extremes in vibrational Fermi resonance coupling behaviors. The Fermi resonance interaction in dicholoromethane is relatively weak, as the unperturbed CH fundamental (ν_1) and CH bend overtone ($2\nu_2$) transitions are separated by about 160 cm^{-1}, while in methanol the corresponding unperturbed transitions (ν_3 and $2\nu_5$, respectively) are nearly degenerate ($\delta \approx 0$). Furthermore, the Fermi coefficient, W, which represents the inherent coupling of the two modes, regardless of their frequency separation, is about twice as large in methanol as in dichloromethane. As a consequence, in dicholoromethane the band arising from the bend overtone (see Figure 1) is about 50 times weaker than the stretch fundamental to which it is coupled, and the separation between the two bands increases monotonically with pressure. In methanol, on the other hand, the two coupled bands are nearly equal in intensity (see Figure 1) and their frequency separation is a nonmonotonic function of pressure. In particular, the observed splitting in methanol goes through a minimum, and

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the intensity ratio of the coupled bands approaches unity at a pressure of 1.25 GPa (10 000 bar), indicating that at this pressure the unperturbed modes become exactly degenerate.

Interestingly, at exact degeneracy the Fermi resonance coupling coefficient, *W*, may be read directly from the spectrum, for at this point *W* is equal to one-half of the observed splitting (δ). Thus, at least in the case of methanol, pressure tuning allows the spectroscopic determination of *W* with little intervening theoretical analysis. The value of *W* determined in this way is shown to be in good agreement with that determined from the pressure variation of *R* and δ away from exact resonance. In both liquids the values of *W* are found to be nearly pressure independent, despite the fact that the observed frequencies and intensities of the Fermi-coupled bands change significantly with pressure.

Previous vibrational Fermi resonance studies[6−18] have employed a variety of experimental and theoretical methods to extract Fermi resonance coupling information from molecular vibrational spectra. These include both infrared and Raman studies of systems in which isotopic substitution[5,7] and/or variations in phase,[14,18] solvent,[8,9,11−13] temperature,[6,7,10,15,16] or pressure[7,10,14−17] have been used to alter the observed Fermi resonance shifts and intensity changes. The key advantage of pressure variation over other methods is that it may be used to continuously vary Fermi coupling over a large range within a given molecule, rather than being restricted to a discrete or more limited range of shifts accessible using isotope, phase, solvent, or temperature variation. A particularly dramatic example of this was recently demonstrated in Fermi resonance studies of ice VII spanning a 50 GPa pressure range, in which the OH stretch and bend overtone were pressure tuned all the way from the preresonance to postresonance regimes, clearly revealing the onset of a strong Fermi resonance at around 25 GPa. In the present work pressure is used in the same way to scan through resonance in liquid methanol (while in liquid CH_2Cl_2 pressure variation probes the postresonant regime).

Two alternative theoretical approaches have been used to interpret the results of previous vibrational Fermi resonance studies. The simplest is a standard perturbative model[1,9,11−17] that relates observed changes in δ and *R* directly to *W* (and the unperturbed intensity ratio, R_0, in cases where this is assumed to be nonzero). The more flexible coupled oscillator model[6−8,10] predicts virtually identical behavior, while including the effects of Fermi resonance on the widths of the coupled bands. The price paid for this flexibility is that higher quality data are required (i.e., including careful line width measurements) in order to accurately determine the larger number of adjustable parameters in this model (typically four parameters must be fit in the coupled oscillator model as opposed to one or two in the perturbative model). We have selected the simpler perturbative model as it has been shown to yield *W* values that are virtually identical to those obtained using the coupled oscillator method.[6,9]

The constancy of the Fermi coupling coefficient, *W*, and anharmonic shift, *x*, is an implicit assumption in most Fermi resonance studies involving variation in isotopic substitution, phase, solvent, temperature, and pressure. On the other hand, some studies suggest that *W* may not remain strictly constant under solvent[6,11] and phase[14] variation. The present pressure dependent study offers a further test of the constancy of *W* and *x*, in addition to illustrating the utility of pressure as a variable in resolving ambiguous vibrational assignments.

II. Experimental Procedures

Spectral grade methanol (CH_3OH) and dichloromethane (CH_2Cl_2) were purchased from Aldrich and used without further purification. The Raman spectra of these liquids, contained in a Merrill-Basset type diamond anvil cell (DAC),[19] were measured using a 10 mW He−Ne laser and microscope-based Raman spectrometer[20] with a 320 mm spectrograph (ISA HR320 f/4.2), equipped with an 1800 gr/mm holographic grating and a 1149 × 256 pixel, liquid N_2 cooled CCD detector (Princeton Instruments LN1152). Measurements were taken at room temperature (23 ± 2 °C) over a pressure range up to 1 GPa in dichloromethane and 2.5 GPa in methanol.

The pressure inside the DAC was determined using the frequency shift of the R1 fluorescence line of ruby chips (~10 μm diameter) immersed in the liquid.[21] The position of the R1 fluorescence and liquid Raman bands were determined using Lorentzian fits to the upper half of the peak (after baseline subtraction). The pressure measurement uncertainty is ±0.05 GPa as determined from variations in R1 fluorescence maximum wavelength (±0.02 nm) for different ruby chips within the same sample.

Relative intensities of Raman bands were obtained either from the peak height (and width), or from direct integration of band areas (as discussed below). Raman frequency shift calibration was performed using neon calibration lamp lines (with a cubic polynomial fit to the frequency as a function of CCD pixel position).[20] The instrumental width (as determined from the full-width-at-half-maximum of neon lamp lines) is 1 cm^{-1}, and the reproducibility of Raman peak positions is better than ±0.5 cm^{-1}.

In general, pressure may induce changes not only in the position and height of Fermi-coupled bands but also in the widths and shapes of the bands. Changes in bandwidth may arise from pressure-induced variations in homogeneous and inhomogeneous line broadening[22] as well as broadening induced by the Fermi resonance interactions.[6,7,23] These effects may be further complicated by the presence of overlapping peaks in the vicinity of the Fermi resonant doublet, as evident around the ν_+ band of methanol (see Figure 1). In addition, intensity integrations are subject to other inaccuracies, as the apparent intensities of small peaks such as the ν_- band of dichloromethane can be very sensitive to baseline subtraction errors. Such complications limit the accuracy with which pressure-induced changes in band intensities may be determined. Thus, in some cases, it may only be possible to accurately determine the integrated intensities of bands over one-half of the band (in which there is less overlap with other peaks). In such cases doubling the half-band integral, assuming the true peaks are perfectly symmetrical, has been used to estimate the total band intensity. In view of the uncertainties associated with peak area measurement, we have also used the ratio of the peak height (or peak height times width), as secondary measures of the intensity ratio of the Fermi-coupled bands.

III. Theoretical Outline

A relation between the observed frequencies, ν_+ and ν_-, and the unberturbed levels, ν_+^0 and ν_-^0, may be obtained from a two level perturbative analysis.[1] The results are most simiply expressed in terms of the frequency separations of the observed, $\delta = \nu_+ - \nu_-$, and unperturbed, $\delta_o = \nu_+^0 - \nu_-^0$, states,

$$\delta_o = [\delta^2 - 4W^2]^{1/2} \tag{1}$$

Note that the above expression assumes that only one fundamental and one overtone are significantly Fermi-coupled. For polyatomic molecules this may often not be strictly true and, in some cases, may even be a very poor approximation. Thus the two-state model must be viewed as a first approximation to the true Fermi-coupling behavior in many polyatomic molecules. This is particularly true for methanol, whose spectra clearly suggest the presence of shoulders representing additional underlying bands in the CH stretch region (see Figure 1 and section V for further discussion).

The Fermi coefficient, W, expresses the inherent coupling strength of the two unperturbed states, while the magnitude of the observed frequency splitting (δ) depends on both W and the separation of the unperturbed levels (δ_o). Thus Fermi coupling may change with pressure even if W is pressure independent, since differential pressure shifts in the unperturbed levels can produce pressure dependent shifts in δ_o. When δ_o is large (as compared to W), the effective Fermi coupling is weak and the observed band positions are very close to those of the unperturbed bands. When δ_o is small, the modes interact more strongly and the observed band splitting may become much larger than δ_o. At exact degeneracy ($\delta_o = 0$) the observed splitting (δ) goes through a minimum, at which point δ becomes exactly equal to $2W$, allowing the direct determination of W from the measured spectrum.

The observed intensity ratio of the coupled bands, $R = I_+/I_-$, can be expressed in terms of δ and δ_o, and the band intensity ratio in the absence of Fermi resonance, R_o.[24,25]

$$R = \frac{I_+}{I_-} = \left\{\frac{(\delta + \delta_o)^{1/2}R_o{}^{1/2} + (\delta - \delta_o{}^{1/2})^{1/2}}{(\delta - \delta_o)^{1/2}R_o{}^{1/2} - (\delta + \delta_o)^{1/2}}\right\}^2 \qquad (2)$$

Note that Since R and δ are experimental observables, W and R_0 are the only two independent variables in eq 2 (since eq 1 defines δ_o as a function of δ and W). Furthermore, since the interaction of interest is between a fundamental mode and an overtone, it is reasonable to assume that the probability of an unperturbed overtone transition is extremely small, and thus R_o may be taken to be equal to infinity or zero (depending on whether the lower or upper frequency unperturbed state derives the overtone), in which case eq 2 simplifies to

$$R = \frac{\delta + \delta_o}{\delta - \delta_o} \quad \text{or} \quad \frac{\delta - \delta_o}{\delta + \delta_o} \qquad (3)$$

This equation (combined with eq 1) allows the determination of W directly from experimentally measured R and δ values (at a single pressure).

$$W = \frac{\delta}{R + 1}\sqrt{R} \qquad (4)$$

Alternatively, given a set of R and δ values determined over a range of pressures, eq 4 may be used to determine the pressure dependence of W (if any). In addition, the dependence of R on δ may be used to aid in assigning the band arising from the overtone (even in cases where the observed intensity of the two coupled bands are comparable), *as the intensity of the band arising from the overtone must, according to eqs 2 and 3, decrease with increasing* δ.

Once δ_o is determined (eq 1), the Fermi resonance induced shift, $\Delta\nu_{fr}$, may be calculated from the following equation

$$\Delta\nu_{fr} = \frac{1}{2}(\delta - \delta_o) = |\nu_+ - \nu_+^0| = |\nu_- - \nu_-^0| \qquad (5)$$

Neglecting off diagonal couplings with other modes, the unperturbed CH bend overtone frequency, ν^0 (whether it be the upper, "+", or lower "−", frequency band), can be expressed in terms of the observed fundamental frequency, ν, and anharmonic shift, x.

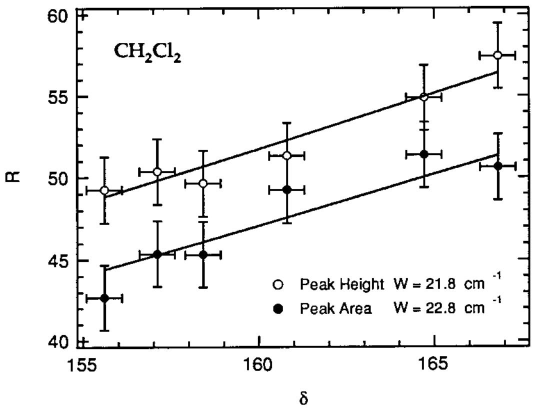

Figure 2. Intensity ratio, R, of the Fermi resonance doublet in CH$_2$Cl$_2$ plotted as a function of the observed peak separation, δ, over a pressure range of $0.001 \le P$ (GPa) ≤ 0.85. Either the peak heights or the peak areas are used to measure the intensity ratio (see text for details), and the Fermi-coupling coefficients, W, obtained from a best fit to eq 4 are shown in the legend.

TABLE 1: Dichloromethane Raman Spectral Data

P (GPa)	ν_+ (cm^{-1})	ν_- (cm^{-1})	ν_2 (cm^{-1})	δ (cm^{-1})	R_1 height ratio	R_2 area ratio
0.0001	2987.4	2831.8	1422.4	155.6	49.25	42.67
0.111	2987.0	2829.9	1421.7	157.1	50.36	45.36
0.14	2987.2	2828.2	1420.7	158.4	49.63	45.31
0.305	2987.9	2827.1	1420.5	160.8	51.32	49.24
0.546	2989.5	2824.8	1418.9	164.7	54.87	51.36
0.847	2990.6	2823.8	1418.2	166.8	57.44	50.63

$$\nu^0 = 2\nu - x \qquad (6)$$

Note that x is thus equal to $2\omega_e x_e$, in terms of the usual cubic anharmonic coefficient for a diatomic normal mode.[1,2] Thus, the anharmonic shift, x, may be determined from the unperturbed overtone frequency, ν^0, and the experimentally measured bend fundamental frequency, ν.

IV. Results

Table 1 contains the measured peak positions of the two coupled bands (ν_- and ν_+) and the bend fundamental (ν_2) in liquid CH$_2$Cl$_2$, as well as the observed splittings, δ, and intensity ratios, R, of the Fermi doublet measured in two different ways (see below), at several pressures (and $T = 23$ °C). The small intensity of the lower frequency band (see Figure 1), as well as the fact that R increases with increasing δ, clearly points to the assignment of the higher frequency band as that arising from CH fundamental in this liquid.

The tabulated values of R have been determined either from the peak heights of the Fermi-coupled bands (R_1) or from the peak areas integrated over the lower frequency half of each band (R_2). Figure 2 shows the resulting R values plotted as a function δ. The lines in Figure 2 represent the predictions of eq 3 (using eq 1), with best fit values of $W = 21.8$ cm^{-1} and $W = 22.8$ cm^{-1} obtained from the R_1 and R_2 data, respectively. Attempts to fit W and R_o simultaneously using eq 2 proved to be less reliable, as covariation of W and R_o could produce fits of nearly equivalent quality, and thus the results were very sensitive to small variations in input data. Equation 3, on the other hand, is more robust and yields W values that are quite insensitive to experimental error (as discussed below).

TABLE 2: Methanol Raman Spectral Data

P (GPa)	ν_- (cm^{-1})	ν_+ (cm^{-1})	δ (cm^{-1})	R_1 height ratio	R_2 area ratio	R_3 height × fwhm ratio	δ_{ave} (cm^{-1})	R_{ave}
0.0001	2835.0	2941.5	106.5	0.63	1.43	1.36	106.6	0.72
0.12	2834.8	2941.2	106.4	0.64	1.42	1.41	106.4	0.73
0.70	2839.9	2945.4	105.5	0.77	1.67	1.71	105.5	0.88
0.87	2842.1	2947.7	105.6	0.79	1.72	1.68	105.3	0.89
1.05	2843.4	2948.5	105.1	0.83	1.90	1.85	105.2	0.96
1.48	2847.6	2952.1	104.9	0.93	2.11	2.01	105.2	1.07
1.83	2849.4	2955.2	105.8	0.99	2.17	2.15	105.5	1.12
2.11	2853.0	2958.8	105.8	1.06	2.37	2.28	105.9	1.21
2.52	2854.7	2961.5	106.7	1.11	2.77	2.21	106.7	1.27

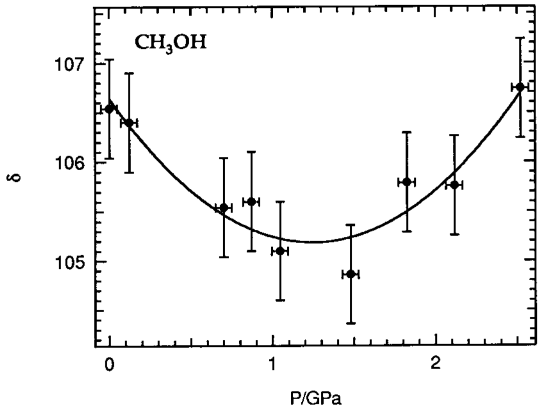

Figure 3. Splitting of the Fermi resonant doublet in CH_3OH goes through a minimum as a function of pressure. The curve is a quadratic fit to the experimentally measured splitting (see eq 7).

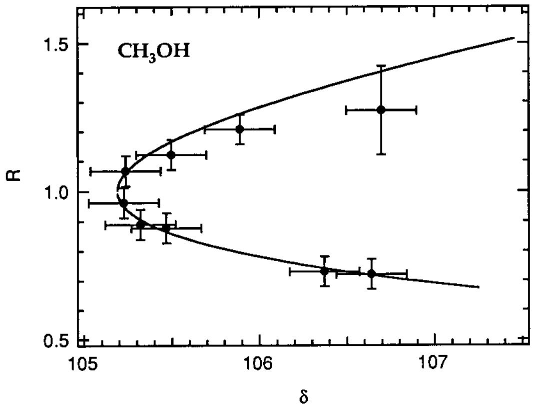

Figure 4. Smoothed experimental data (points) for the intensity ratio, R_{ave}, and splitting, δ_{ave}, of CH_3OH compared with the prediction of eq 3 (curve). The value of $W = 52.6$ cm^{-1} is obtained from the minimum splitting ($\delta = 105.19$ cm^{-1}, which occurs at $P = 1.25$ GPa, see Figure 3).

The good agreement between the theoretical and experimental results shown in Figure 2 suggests that W is relatively insensitive to pressure. A more quantitative measure of the pressure dependence of W may be obtained by compairing W values obtained at different pressures (using eq 4). The results confirm that W is constant to within experimental error over the experimental pressure range, with a total (random) variation in W of 21.8 ± 0.3 and 22.8 ± 0.5 cm^{-1} when fitting the R_1 and R_2 data, respectively. Thus the average value of $W \approx 22.3$ cm^{-1} is within the estimated experimental error of the two methods.

Table 2 contains the experimental peak positions of the Fermi-coupled bands (ν_- and ν_+) in liquid CH_3OH, as well as δ and R values measured as a function of pressure (at $T = 23$ °C). Three methods were used to estimate the intensity ratio, R, in this liquid; (i) peak height (R_1), (ii) integrated area (R_2), and (iii) peak height times the full width at half-maximum (fwhm) (R_3). In addition, better averaged experimental values, δ_{ave} and R_{ave}, have been obtained by smoothing the experimental results as described below. The assignment of the two Fermi-coupled peaks appearing in the Raman spectrum of CH_3OH is not as obvious as it was in CH_2Cl_2, since in this case the two coupled bands are nearly equal in intensity. However, the assignment is clarified by the observation that R increases while δ decreases at low pressures, indicating that the lower frequency mode appearing in the low-pressure spectra must arise from the fundamental. At the highest pressure, on the other hand, R increase with increasing δ, and so in this regime the higher frequency mode derives from the fundamental. In other words, it is evident that *a crossing of the two unperturbed modes occurs as a function of pressure in liquid methanol.*

When the two unperturbed states are exactly degenerate ($\delta_o = 0$) the observed splitting between the Fermi-coupled bands goes through a minimum, as shown in Figure 3. A quadratic fit to δ as a function of P (see Figure 3 and eq 7) suggests that the coordinates of the minimum occur at a pressure of 1.25 GPa, where $\delta = 105.19$ cm^{-1}. This quadratic fit may also be used to smooth the experimental data, yielding a more accurate estimate of the true splitting as a function of pressure (see δ_{ave} in Table 2).

$$\delta_{ave} = 106.64 - 2.3273P + 0.93224P^2 \qquad (7)$$

According to eq 1, at the point where δ is a minimum (and thus $\delta_o = 0$) the value of W should be simply equal to one-half of the observed splitting, $W = \delta/2 = 52.6$ cm^{-1} (at $P = 1.25$ GPa). Furthermore, according to eq 3, at this pressure the two coupled peaks should also have exactly equal intensities, $R = 1$. The experimental intensity ratios (R_1, R_2, and R_3 in Table 2) are indeed all very close to 1; however, the uncertainty in the measured R values is too great to allow a critical test of the predicted coincidence of the minimum in δ with the point at which R is exactly equal to 1. On the other hand, if it is *assumed* that the true R value is equal to 1 at the point where δ is a minimum, then a scaling factor relating the experimental intensity ratios, R_i, to the true ratio, R, may be determined. In other words, a constant, C_i, may be found such that $R = C_iR_i = 1$ at $P = 1.25$ GPa. In practice this has been done by fitting the experimental R_i vs pressure data to a quadratic, and then scaling the quadratic so as to fulfill the above constraint. The resulting scaling factors, $C_1 = 1.114$, $C_2 = 0.518$, and $C_3 = 0.520$, have in turn been used to correct the experimental R_i values, and the average of the resulting three R values is reported in Table 2 as R_{ave} (the three scaled values of R are found to agree with each other to within ±0.05 at all but the highest pressure, where they are within ±0.15 of R_{ave}).

Figure 4 shows a plot of the smoothed experimental data, R_{ave} and δ_{ave}, along with a curve representing the predictions of eq 3 (using eq 1). Note that the curve in Figure 4 is not

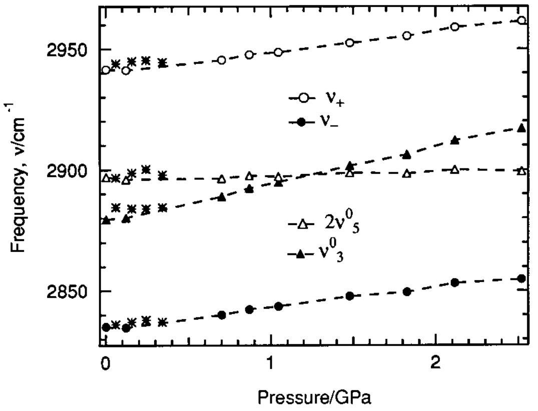

Figure 5. Experimental Raman peak positions (open and filled circles) and the associated unperturbed frequencies (triangles) in CH_3OH plotted as a function of pressure (the lines connect the experimental points). The asterisked points (*) represent previously published results[23] for CH_3OH as a function of pressure.

derived from a fit to the experimental data in this figure, but simply from the minimum value of δ (which yields $W = 52.6$ cm^{-1}, as described above). The good agreement between the experimental and theoretical results suggests not only the appropriateness of eq 3 in describing the Fermi resonance in this system, but in addition, that W is effectively independent of pressure (within experimental error) even over the large pressure range of our CH_3OH data (0.0001 GPa $\leq P \leq$ 2.51 GPa). More quantitative bounds on the variation of W with pressure may again be obtained from eq 4 using the values R_{ave} and δ_{ave} at each pressure. The resulting maximum deviation in W occurs at the highest pressure, where the best fit value of W is only about 0.3 cm^{-1} above the mean value, $W = 52.65$ cm^{-1}, while at all the other pressures W is within about 0.1 cm^{-1} of the mean value. Since the highest pressure point is also the one with the greatest experimental uncertainty, the apparently larger deviation of this point from the curve in Figure 4 does not necessarily indicate a significant pressure-induced change in W.

Figure 5 shows the pressured dependence of the measured Fermi-coupled states (ν_- and ν_+) and the calculated unperturbed states (ν_3^0 and $2\nu_5^0$) in liquid methanol. The data points marked by asterisks (*) represent the results of Zerda et al.,[23] obtained using a coupled oscillator method to evaluate Fermi interactions as a function of pressure (from 0.06 to 0.34 GPa at 0 °C). Clearly, there is good agreement between the two sets of experimental results, although Zerda's data cover a lower pressure range (and pertains to a lower temperature).

The anharmonic shift, x, of the bending fundamental of dichloromethane may be determined using eq 6, along with the experimentally measured frequency given in Table 1. This yields an anharmonic shift of $x = -10.0 \pm 0.5$ cm^{-1} (assuming $W = 22.3$ cm^{-1}) with no systematic pressure variation. This value is slightly larger than the $x = -7.3$ cm^{-1} reported for gaseous dichloromethane.[26] Thus, although there appears to be a small difference between the anharmonicity in the gas and liquid phases, there is clearly no significant pressure dependence of the anharmonicity in the high-pressure liquid, which is consistent with the behavior inferred from other high-pressure studies in liquids and solids.[27,28]

Determination of the anharmonicity of the bending mode in methanol is complicated by the presence of three bands appearing within 25 cm^{-1} of each other in the bend fundamental region in the gas phase.[29] The band with the lowest frequency is the ν_5 symmetric bend, which appears at 1455 cm^{-1} in the gas phase.[29] Our liquid Raman spectra reveal at least two broad overlapping bands in the bend region with approximate peak positions of ~1452 and ~1470 cm^{-1} at 1 atm. If the lowest of these is assumed to be ν_5, then an anharmonic shift of near -10 cm^{-1} would be required in order to match the unperturbed overtone frequency in the liquid phase (see Figure 5 and section V). If the higher mode were ν_5, then an anharmonic shift of roughly -40 cm^{-1} would be implied. Thus the lower frequency bend fundamental in the liquid phase is most likely ν_5, both because it yields an anhamonicity close to that of the CH bend in CH_2Cl_2 and because ν_5 is the lowest frequency bend in the gas phase. Accurate determination of the pressure dependence of the bend anharmonicity is hampered by increasing overlap in the bend fundamental region, which merges into a single broad peak with increasing pressure.

V. Discussion

The two-state model used to analyze the high-pressure Fermi resonance behavior in liquid methanol and dichlormethane clearly involves significant approximations. On one hand the unpertubed bend overtone is assumed to have zero intensity in deriving eqs 3 and 4. More significantly, other fundamentals, overtones, and combination bands, which may well contribute to the spectra of methanol in the CH stretch region, have been neglected. The existence of these additional bands is evidenced not only by the shoulders appearing in Figure 1 but also by detailed gas and matrix isolation IR studies of methanol, which identify a total of three fundamentals and four overtones or combination bands in the CH stretch region, all of which have the same symmetry as the CH stretch fundamental, and so may contribute to the observed Fermi resonance.[29] In the gas phase IR spectra all of these bands appear as more or less separate peaks, while in the liquid phase IR and Raman spectra only two prominent bands appear in this region (although these show evidence of being composite bands). Our assumption that the stretch fundamental is the most strongly perturbed by Fermi resonance is supported by Halonen's recent detailed analysis of the gas-phase IR spectra.[30] However, our suggestion that the $2\nu_5$ is the only overtone or combination band that is significantly coupled to ν_3 is clearly a simplification. Thus, although the true situation is more complex than suggested by the two-state model, the width of the bands and the very small intensity and frequency differences involved preclude a more detailed analysis of the high-pressure methanol data.

Comparison of the two liquids indicates that the Fermi resonance coupling coefficient is about twice as large in CH_3OH as it is in CH_2Cl_2: $W = 22.3$ cm^{-1} in CH_2Cl_2 and $W = 52.6$ cm^{-1} CH_3OH. These values are in very good agreement with those previously reported for these two molecules: $W = 23.0$ cm^{-1} obtained from gas-phase CH_2Cl_2 data[26] and $W = 53.5$ cm^{-1} for liquid CH_3OH.[9] The good agreement between the high-pressure liquid and gas-phase values of W suggests that *W is insensitive to pressure over the entire gas to high-pressure liquid density range*.

On the other hand, the Raman spectrum in the high-pressure solid phase of dichloromethane, where $\delta \approx 100$ cm^{-1} and $R \approx 189$, yields a Fermi-coupling coefficient of $W \approx 18.7$ cm^{-1} (about 4 cm^{-1} below that in the gas and high-pressure liquid). Thus it appears that there is a small but measurable difference between W in the liquid and solid phases. Such a change in W is consistent with previous work by Bertran and co-workers suggesting changes in W in different solvents[11] or even in different phases.[14] Thus, although W is found to be relatively insensitive to pressure in the fluid phase, caution should be exercised in accepting the often assumed constancy of W under changes in phase or solvent.

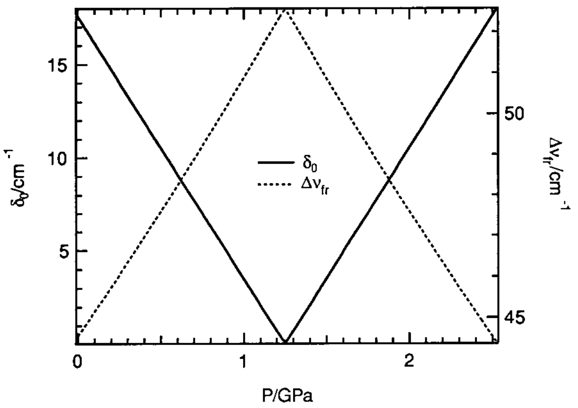

Figure 6. Experimentally derived unperturbed state splitting, δ_o, and Fermi resonant shift, $\Delta\nu_{fr}$, plotted as a function of pressure (see text for details).

The splitting of the unperturbed states, δ_o, in the two liquids may be obtained from eq 1 using the values of *W* derived above, and the experimental splittings, δ. In dichloromethane the unperturbed state splitting is very close to the observed state splitting ($\delta_o \approx \delta - 6$ cm^{-1}: $\nu^0{}_+ \approx \nu_+ - 3$ cm^{-1}, $\nu^0{}_- \approx \nu_- + 3$ cm^{-1}), as expected since the states are far from resonance and *W* is relatively small. In methanol, the unperturbed splitting is near zero and so most of the observed splitting is due to Fermi resonance. Figure 6 displays a plot of δ_o and the Fermi resonance shift, $\Delta\nu_{fr}$, in methanol, calculated from the smoothed experimental splitting, δ_{ave} (eq 7), and eqs 1 and 4. Note that the approximately linear pressure dependence of δ_o and $\Delta\nu_{fr}$ (shown in Figure 6) contrasts with the nonlinear pressure dependence of the δ values from which these were derived (as shown in Figure 3). On the other hand, the nearly linear pressure dependence of δ_o and $\Delta\nu_{fr}$ is consistent with the typically linear pressure shift of vibrational frequencies in liquids at high pressures,[19] as well as with similar behavior observed in high-pressure Fermi resonance studies of ice.[17]

VI. Conclusions

Pressure variation is shown to offer a convenient and reliable way to resolve ambiguities in spectral assignments and extract quantitative Fermi resonance coupling information from Raman spectra, using a simplified two-state model. Pressure variation offers an ideal method for carrying out such measurements, as it may be used to continuously vary the splitting between unperturbed states within a molecule without resorting to solvent or isotope dependent measurements (which may introduce additional perturbations beyond the Fermi interactions of interest).

Caution should be exercised in taking the results of the present two-state Fermi resonance analysis too literally. In particular, the underlying spectroscopic structure in the CH stretch region of methanol is clearly more complex than suggested by the two-state model. Given the more detailed understanding of the complex vibrational spectroscopy of this molecule in the gas phase and in matrix isolation,[29,30] it would be very appealing to attempt a reinterpretation of the liquid-phase data using a more sophisticated multilevel Fermi coupling analysis.

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