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# Isotopic dilution, self-association, and Raman non-coincidence in the binary system (CH<sub>3</sub>)<sub>2</sub>CO+(CD<sub>3</sub>)<sub>2</sub>CO reinvestigated by polarized Raman measurement and ab initio calculations

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# Isotopic dilution, self-association, and Raman non-coincidence in the binary system $(\text{CH}_3)_2\text{C}=\text{O} + (\text{CD}_3)_2\text{C}=\text{O}$ reinvestigated by polarized Raman measurement and ab initio calculations

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Dedicated to Professor Bernhard Schrader

## Abstract

Raman spectra of the binary system  $(\text{CH}_3)_2\text{C}=\text{O}$  (acetone) +  $(\text{CD}_3)_2\text{C}=\text{O}$  (acetone- $\text{d}_6$ ) were reinvestigated employing a more precise and sensitive scanning multichannel detection scheme. The  $I_{\parallel}$  and  $I_{\perp}$  components of the Raman scattered radiation were recorded in the C=O stretching region, 1600–1800  $\text{cm}^{-1}$  as well as in the C–D and C–H stretching regions, 2000–2300 and 2800–3100  $\text{cm}^{-1}$ , respectively, in different mixtures with the varying mole fractions of the reference system. A careful Raman line shape analysis yielded after fit  $\Delta\nu_{\text{nc}}$  due to Raman non-coincidence effect (NCE) in acetone and acetone- $\text{d}_6$  as  $4.87 \pm 0.01$  and  $4.49 \pm 0.01$   $\text{cm}^{-1}$ , respectively. The optimized geometries and wavenumbers of the neat acetone molecule and its self-associated structure were calculated using ab initio method at the MP2 level using 6-31++G(d,p) basis set. The influence of self-association and NCE together were examined. A systematic study of Raman line shape analysis led to a hitherto unexplored aspect, the wavenumber shift and linewidth variation of the  $\nu_1(\text{C–H})$  stretching mode of acetone upon isotopic dilution. The linewidth variation with the mole fraction of the reference system shows an excellent agreement with the corresponding linewidths derived from the  $T_2$  values obtained by three color fs-CARS study reported earlier.

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**Keywords:** Isotopic dilution; Raman spectra; Self-association; Raman non-coincidence; Ab initio calculations

## 1. Introduction

A systematic study of symmetric modes in polar liquids has engaged considerable attention of

spectroscopists for more than one decade, especially to understand the non-coincidence effect (NCE) in the Raman spectra of polar liquids [1]. The phenomenon of non-coincidence arising in the measurement of the polarized Raman spectra of molecular liquids, associated with symmetric modes of polar molecules, is well known and has extensively been studied [2–7]. The non-coincidence causes a wavenumber difference

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between the anisotropic and isotropic parts of the Raman scattering and it is defined as:

$$\Delta\nu_{\text{nc}} = \nu_{\text{aniso}} - \nu_{\text{iso}}, \quad (1)$$

where  $\nu_{\text{aniso}}$  and  $\nu_{\text{iso}}$  are the peak wavenumbers of the anisotropic and isotropic parts, respectively. This effect is caused owing to the interaction between the permanent dipoles of the neighboring polar molecule, which mainly originate from the highly polar character of the bonds and they get aligned anisotropically (on thermal average) to some extent in the liquid. The stretching vibration of a polar bond in these molecules is coupled by the transition dipole coupling mechanism. The resonant transfer of vibrational excitation energy between the molecules coupled by permanent dipole moment, hydrogen bonds or any other interactions thus cause the NCE.

Although Wang and McHale [8], McHale [9,10], Mirone and Fini [11], Mirone [12] had done a good deal of theoretical work on NCE, Logan [1] presented a most comprehensive theory, which is still probably the most acceptable and adequate quantitative theoretical model for the interpretation of the experimental results on NCE. Torii [13] made a critical examination of various approximate theories of Raman NCE in the light of Monte Carlo simulation. It was argued that when the transition dipole is parallel to the permanent dipole,  $\nu_{\text{iso}}$  turns out to be lower than  $\nu_{\text{aniso}}$ . However, a quantitative understanding of the Raman NCE was not complete. The acetone was mostly taken as a model system to test the various theories of NCE, but there have been large disagreements. For example, McHale's [9] theory yields a value of  $\Delta\nu_{\text{nc}}$  defined by Eq. (1), which is smaller by an order of magnitude, whereas Logan's theory [1], which is based on the mean spherical approximation [14], usually yields values of  $\Delta\nu_{\text{nc}}$  that are in much better agreement with the experimental results [3,11,15].

Mirone and coworkers [16–18] probably reported the first experimental observation of Raman NCE. Acetone and acetone- $\text{d}_6$  are the model systems where a higher polar bond C=O exists and a number of studies [16–19] have been made on this system. In a Raman study on the intermolecular coupling of the C=O stretching vibration in liquid methyl acetate and acetone was made by Dybal and Schneider [19] and they studied mainly the isotopic mixtures of acetone- $\text{O}^{16}$  and acetone- $\text{O}^{18}$ , where the C=O stretching

vibrations differed by  $\sim 30 \text{ cm}^{-1}$ , but the near-resonant vibrational coupling between the stretching vibrations of  $\text{C}=\text{O}^{16}$  and  $\text{C}=\text{O}^{18}$  did not show any appreciable change in the value of  $\Delta\nu_{\text{nc}}$ . Later Torii [13] also selected  $(\text{CH}_3)_2\text{C}=\text{O}$  for critical comparison of the existing theories [8–10,20]. Wallen et al. [21] again selected the C=O stretching mode of the liquid acetone, but in their study, the molecules were confined to porous silica glasses prepared by the sol–gel process.

Bhattacharjee et al. [22] once again selected the C=O stretching Raman band of acetone for studying the NCE in polar liquids, but they focused their attention on binary mixtures in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  and compared the experimental results with the theoretical values predicted by dipole and resonant transfer model [16–18] and mean spherical approximation approach [14] adopted by Logan [1]. Musso et al. [23] studied the NCE for the C=O stretching band of  $(\text{CH}_3)_2\text{C}=\text{O}$  in a highly diluted mixture of  $(\text{CH}_3)_2\text{C}=\text{O} + \text{CCl}_4$  where the emphasis was directed mainly towards the NCE in such a diluted regime which was not accessed in the earlier studies. In yet another study [24], the major emphasis was laid down on comparison of the Monte Carlo simulation results with the experimental results. Recently Giorgini et al. [25] have examined an interesting aspect, whether benzene may be effective in promoting the sign inversion of the NCE of C=O stretching mode of acetone in the high dilution regime as claimed in the study by Kecki and Sokolowska [26].

The self-association, which is caused due to hydrogen bond formation between two like molecules in neat liquid and slowly weakens in a binary mixture, was examined in an isotopic mixture  $\text{CH}_3\text{C}\equiv\text{N} + \text{CD}_3\text{C}\equiv\text{N}$  [27] as well as in the binary mixture  $\text{C}_6\text{H}_5\text{C}\equiv\text{N} + \text{CH}_3\text{OH}$  [28] recently. The Raman line shape corresponding to the stretching mode of a highly polar bond C $\equiv$ N is influenced considerably by self-association in both the cases. In the first study on isotopic mixtures of  $\text{CH}_3\text{C}\equiv\text{N} + \text{CD}_3\text{C}\equiv\text{N}$ , the double peak nature of the Raman band corresponding to  $\nu_2(\text{C}\equiv\text{N})$  stretching was explained in terms of self-association. In the second study [28] on  $\text{C}_6\text{H}_5\text{C}\equiv\text{N}$ , in the neat liquid as well as in the binary mixtures with  $\text{CH}_3\text{OH}$  having different molar ratios, spectral features could be explained satisfactorily in terms of self-association and intermolecular hydrogen bond,

$\text{C}_6\text{H}_5\text{C}\equiv\text{N}\cdots\text{H}-\text{OCH}_3$  formation. Both these aspects seem to have been either ignored completely or, at least, not adequately addressed to in the case of recent studies [22–26] on  $(\text{CH}_3)_2\text{C}=\text{O}$  for the  $\text{C}=\text{O}$  stretching vibration, either in the neat liquid or in the binary mixtures.

In view of the foregoing discussion and the two recent studies [27,28], it was thought worthwhile to make an isotopic dilution (ID) study on the binary system  $(\text{CH}_3)_2\text{C}=\text{O} + (\text{CD}_3)_2\text{C}=\text{O}$  as a function of concentration in mole fraction of the reference system, to study the self-association caused due to hydrogen bonding between O atom of the  $\text{C}=\text{O}$  group of one molecule with the H/D atom of another  $(\text{CH}_3)_2\text{C}=\text{O}/(\text{CD}_3)_2\text{C}=\text{O}$  molecule and to understand the observed spectral changes. Ab initio calculations [29,30] were also performed with a view to establish a correlation between the experimentally observed spectral features and calculated optimized geometries as well as wavenumbers of the normal modes. The wavenumber shifts and linewidth variations of the  $\nu_1(\text{C}-\text{H})$  vibration of acetone were also examined in the present study and the variation of the linewidth with concentration was compared with the results obtained from the study of dephasing rate in time domain [31].

## 2. Experimental details and results

Raman spectra were recorded using a SPEX 1404 double monochromator (2400 g/mm) and a CCD-Camera (Photometrics model SDS 9000) and scanning multichannel detection scheme. For recording the spectrum, excitation at 514.5 nm from an  $\text{Ar}^+$ -Laser (Spectra Physics) was used. The laser power at the sample was 300 mW. The  $I_{\parallel}$  and  $I_{\perp}$  components were obtained by overlapping of three recordings and isotropic and anisotropic parts were calculated using the relationships:

$$I_{\text{iso}} = I_{\parallel} - (4/3)I_{\perp} \quad (2)$$

and

$$I_{\text{aniso}} = I_{\perp}. \quad (3)$$

The polarization arrangement was adjusted by using one Glan-Taylor polarizer and double Fresnel rhomb for polarization rotation before the sample and one

Glan-Taylor polarizer at the entrance slit. The sample was kept in a rotating quartz cell and  $90^\circ$  scattering geometry was used for collecting the Raman scattered radiation. Acetone and acetone- $\text{d}_6$  were obtained from Aldrich and were used without further purification. All measurements were carried out at room temperature.

The entrance slit of the double monochromator was kept constant at 100  $\mu\text{m}$  for all the measurements and this gives a resolution of  $\sim 1.5 \text{ cm}^{-1}$ . It was quite evident from the quality of the spectra that the S/N ratio was reasonably high ( $>40$ ). The spectra have been recorded by accumulating the signal for 30 s in the  $\nu(\text{C}=\text{O})$  stretching region and 10 s in the  $\nu(\text{C}-\text{H})$  stretching region per single window. One single window covers  $\sim 100$  and  $80 \text{ cm}^{-1}$  in the  $\nu(\text{C}=\text{O})$  and the  $\nu(\text{C}-\text{H})$  stretching regions, respectively. In order to take advantage of the sensitivity of the scanning multichannel technique (SMT), which was already employed in earlier studies [3,27,28], every data point was generated by an overlap of two frames.

The isotropic parts of the Raman spectra in the  $\text{C}=\text{O}$  stretching region were obtained from the measured  $I_{\parallel}$  and  $I_{\perp}$  components using Eq. (2) for the neat liquids, acetone and acetone- $\text{d}_6$ , as well as for different mixtures having mole fractions of  $(\text{CH}_3)_2\text{C}=\text{O}$  with the values  $x = 0.2, 0.4, 0.6$ , and  $0.8$ . The spectra thus obtained were fitted to two peaks in case of the neat liquids and to four peaks in case of the mixtures. The band shape function used in the fitting was always a mixture of Lorentzian and Gaussian profiles, for which an initial guess value was given. The fit always yielded a final value for the ratio between Lorentzian and Gaussian type function and this was almost independent of the initial guess. Thus in effect the band shape function used in the fitting closely resembles a Voigt profile similar to earlier studies [3,27,28]. The isotropic parts of the measured spectra (thin lines), the fitted Raman line profile (thick lines) as well as the individual peaks as resulted from the fit (dotted lines) are presented in Fig. 1.

The isotropic and anisotropic parts of the Raman spectra of the  $\text{C}=\text{O}$  stretching vibration in neat  $(\text{CH}_3)_2\text{C}=\text{O}$  and  $(\text{CD}_3)_2\text{C}=\text{O}$  as well as their mixtures with varying mole fractions as obtained from the measured  $I_{\parallel}$  and  $I_{\perp}$  using the above relationships are presented in Fig. 2. The wavenumbers of the Raman

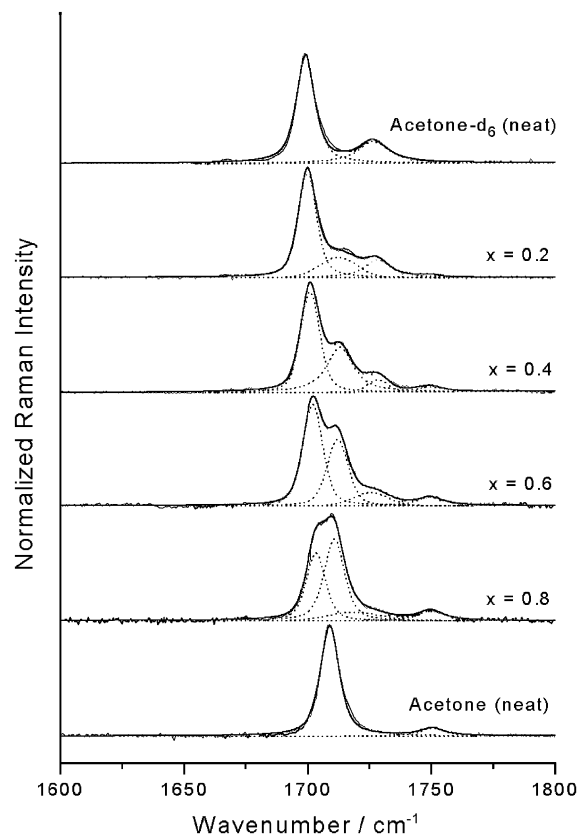


Fig. 1. Isotropic part of the Raman spectra in the C=O stretching region, 1600–1800 cm<sup>-1</sup> for neat acetone and acetone-d<sub>6</sub> and four other isotopic mixtures with mole fraction of acetone,  $x = 0.2, 0.4, 0.6, 0.8$ .

peaks corresponding to C=O stretching vibration of (CH<sub>3</sub>)<sub>2</sub>C=O and (CD<sub>3</sub>)<sub>2</sub>C=O are at ~1709 cm<sup>-1</sup> and at ~1699 cm<sup>-1</sup>, respectively. These two values differ by ~10 cm<sup>-1</sup>. The isotropic and anisotropic components of the C=O stretching vibration of (CH<sub>3</sub>)<sub>2</sub>C=O and (CD<sub>3</sub>)<sub>2</sub>C=O in neat liquids are separated by 4.87 (±0.01) and 4.49 (±0.01) cm<sup>-1</sup>, respectively, as determined from the fits and are depicted in Fig. 2. These separations were obtained from the fitted peak functions for the isotropic and anisotropic parts.

The isotropic part of the Raman spectra of the  $\nu_1$ (C–H) stretching region, 2800–3100 cm<sup>-1</sup> and  $\nu_1$ (C–D) stretching region, 2000–2300 cm<sup>-1</sup> were also obtained as mentioned above. The  $\nu_1$ (C–H) stretching vibration, which was observed at

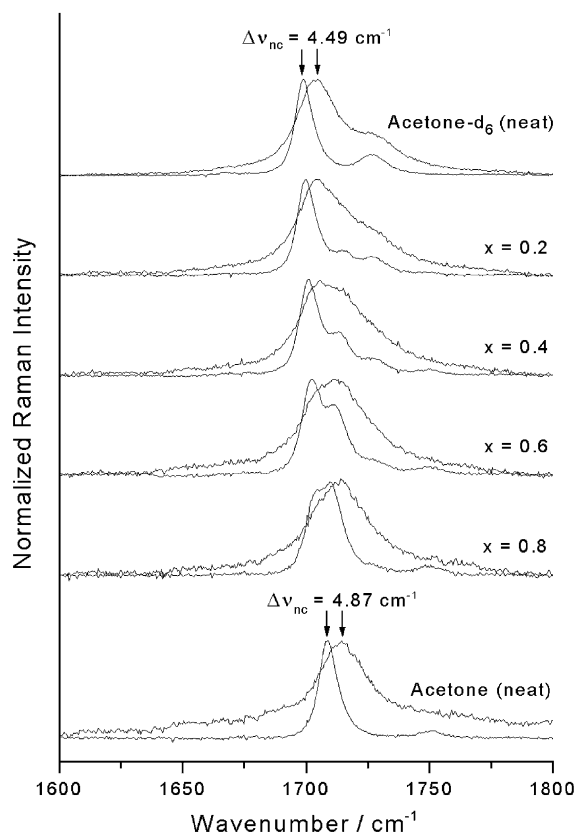


Fig. 2. Isotropic and anisotropic parts of the Raman spectra in the same region and for the same concentrations as in Fig. 1, with the difference that  $\Delta\nu_{nc}$  due to Raman non-coincidence effect (NCE) are also depicted for neat acetone and acetone-d<sub>6</sub>.

~2924 cm<sup>-1</sup> in neat liquid, exhibits some regular, but interesting behavior. The isotropic part of the spectra in the region 2800–3100 cm<sup>-1</sup> for the neat acetone and different isotopic mixtures were obtained from the measured  $I_{||}$  and  $I_{\perp}$  using the above relationships and they are presented in Fig. 3. The  $\nu_1$ (C–D) stretching vibration was observed at 2109.5 cm<sup>-1</sup>. However, we mainly concentrated on  $\nu_1$ (C–H) stretching vibration only.

### 3. Calculation of geometries and vibrational wavenumbers

In order to understand the phenomenon of self-association and its relationship to the spectral features,

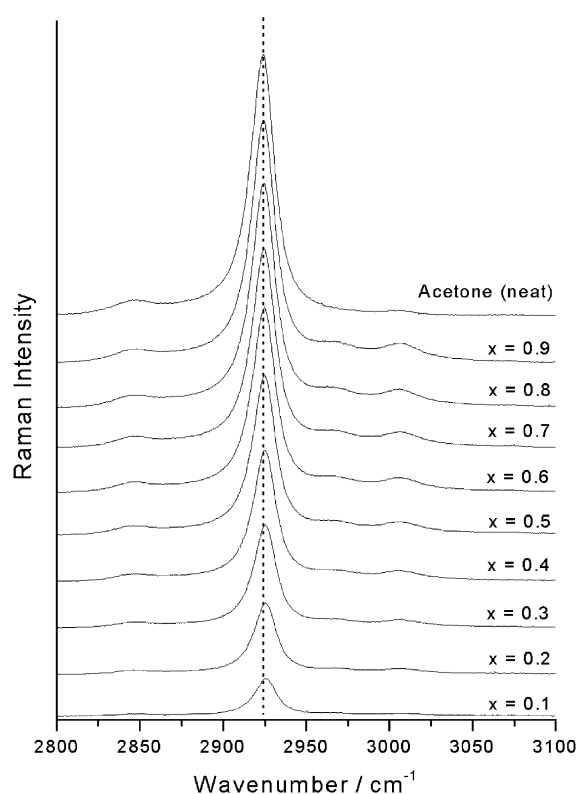


Fig. 3. Isotropic part of the Raman spectra in the C–H stretching region, 2800–3100  $\text{cm}^{-1}$  for neat acetone and nine other isotopic mixtures with mole fraction of acetone,  $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ .

the ground state geometries for  $(\text{CH}_3)_2\text{C}=\text{O}$  and its dimer were optimized by the gradient procedure at the second order level of closed shell Møller–Plesset (MP2) perturbation theory employing the 6-31++G(d,p) basis set. The wavenumbers of the different normal modes were computed at the MP2 level of ab initio theory [30] with the GAUSSIAN 98 program (revision A.9) [31]. The optimized geometries obtained from the ab initio calculations for the monomer as well as for the self-associated dimer structure are presented in Fig. 4. The vibrational wavenumber calculations also help to ensure that the stationary points located on the potential energy surface were really the global minima.

A closer examination of the structures of the monomer (Fig. 4(a)) and self-associated dimer reveals that the C=O bond length slightly increases from

1.231 Å in the monomer to 1.233 Å in the self-associated structure. Thus the influence of self-association is small, but not insignificant. The O···H bond length of the hydrogen bond formed between the O atom of one  $(\text{CH}_3)_2\text{C}=\text{O}$  molecule and an H atom of the  $\text{CH}_3$  group of the other  $(\text{CH}_3)_2\text{C}=\text{O}$  molecule has been obtained from the geometry optimization to be 2.434 Å, which is usual for a hydrogen bond of medium strength. However, a hydrogen bond of the type shown in Fig. 4(b) obviously reduces the bond strength of the polar bond C=O leading to a reduced force constant and thereby causing a lowering of the wavenumber. The vibrational wavenumber calculated for the C=O stretching vibration in  $(\text{CH}_3)_2\text{C}=\text{O}$  and  $(\text{CD}_3)_2\text{C}=\text{O}$  turns out to be 1761.6 and 1751.3  $\text{cm}^{-1}$ , respectively. It is a well known fact that ab initio calculations [29,30] yield a higher value for the wavenumbers of the normal modes as compared to the experimental values and a scaling factor has to be used. A scaling factor of 0.9702 reproduces quite nicely the observed wavenumbers of C=O stretching vibration both in acetone and acetone- $\text{d}_6$ , at 1709.0 and at 1699.1  $\text{cm}^{-1}$ , respectively.

#### 4. Wavenumber shifts of the C=O stretching vibrations upon isotopic dilution

The wavenumber shifts ( $\Delta\nu$ ) for the different vibrations of a molecule upon ID have drawn considerable attention over almost two decades and particularly interesting is the change of  $\Delta\nu$  upon isotopic mixing [3,27,32–35]. In a very early study [32] on the isotopic mixture  $\text{C}_6\text{H}_6 + \text{C}_6\text{D}_6$ , the major emphasis was on demonstrating the potentiality of the then recently developed technique [36] of four-channel Raman difference spectroscopy (RDS) for measuring small ( $0.35 \pm 0.04 \text{ cm}^{-1}$ ) wavenumber shifts. Later Meinander et al. [33] studied two isotopic mixtures  $\text{C}_6\text{H}_6 + \text{C}_6\text{D}_6$  and  $\text{C}_5\text{H}_5\text{N} + \text{C}_5\text{D}_5\text{N}$  at three different mole fractions ( $x = 0.25, 0.5$ , and  $0.75$ ) of the reference system for several vibrational modes and attempted to explain the concentration dependence of both wavenumber and linewidth of a Raman band in terms of intermolecular interactions for which a theory was proposed by Logan [37]. But the emphasis was still more directed on determining

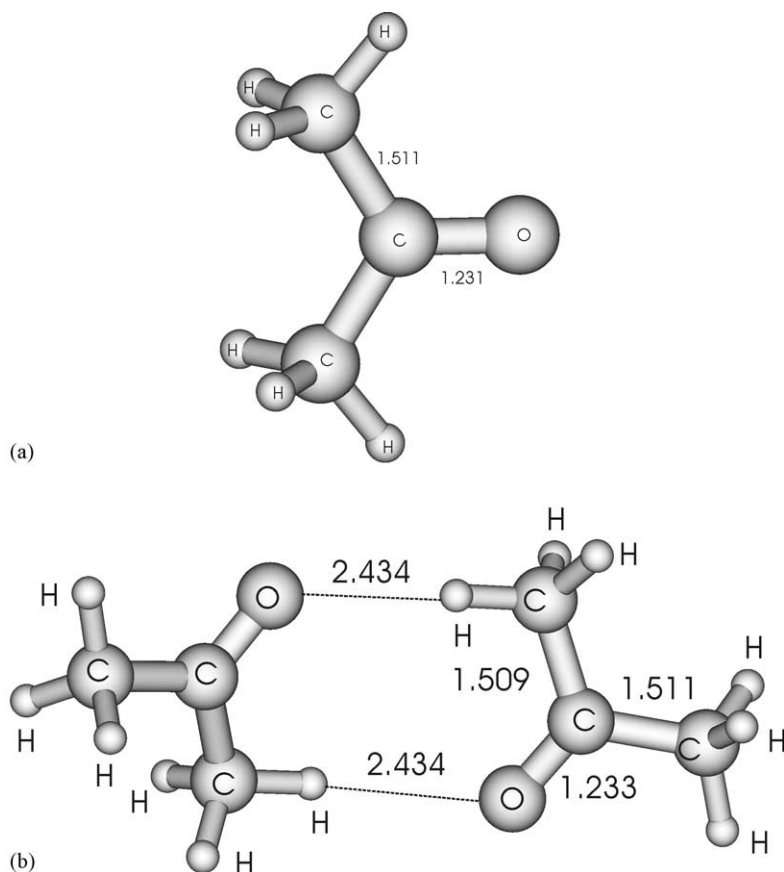


Fig. 4. Optimized geometries obtained by ab initio calculations for (a) monomer of acetone; (b) self-associated dimer of acetone (the numbers refer to interatomic distances in Å).

the small wavenumber shifts of  $\sim 0.2 \text{ cm}^{-1}$  with high precision by employing the technique of RDS [32,33].

Kamogawa and Kitagawa [34] probably made the first serious and systematic effort to understand the concentration dependence of the wavenumber shifts in two isotopic mixtures, C<sub>6</sub>H<sub>6</sub> (B-h) + C<sub>6</sub>D<sub>6</sub> (B-d) and CH<sub>3</sub>C≡N (AN-h) + CD<sub>3</sub>C≡N (AN-d). Although a new device for RDS was also introduced in this study [34], the main emphasis was to explain the concentration dependence of wavenumber shift upon ID. The totally symmetric Raman modes ( $\nu_1$ (C-H) of AN-h and AN-d;  $\nu_2$ (C-H) and  $\nu_7$ (C-H) degenerate mode of B-h and B-d) were studied in detail. Although the plot of the wavenumber shifts vs. concentration/mole fraction of the reference system usually exhibited a linear dependence, the  $\nu_2$ (C-D) and degenerate  $\nu_7$ (C-D) modes of B-d showed an

abrupt change at extreme dilution. The  $\nu_1$ (C-H) of AN-h and  $\nu_1$ (C-D) of AN-d were studied recently [27] and relatively precise values of wavenumber shifts were reported. The phenomenon of self-association in AN-h/AN-d was also studied [27] using ab initio methods [29,30] and Raman line shape analysis of the  $\nu_2$ (C≡N) stretching mode of AN-h/AN-d.

As described earlier, and as depicted in Fig. 1, the measured Raman line profiles in the C=O stretching region were fitted to two and four profiles for neat liquids (acetone and acetone-d<sub>6</sub>) and isotopic mixtures, respectively. The vibrational wavenumbers for the  $\nu$ (C=O) stretching of both (CH<sub>3</sub>)<sub>2</sub>C=O and (CD<sub>3</sub>)<sub>2</sub>C=O obtained from fit are depicted as a function of mole fraction of acetone in Fig. 5. It is evident from this figure that  $\nu$ (C=O) shows an upshift



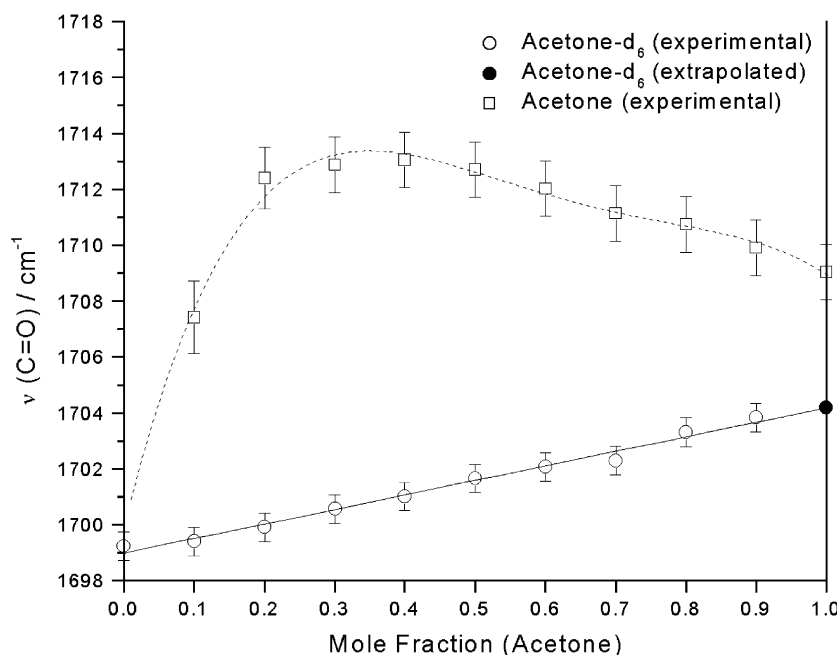


Fig. 5. The wavenumber positions of the  $\nu(\text{C}=\text{O})$  stretching vibration in acetone and acetone- $\text{d}_6$  obtained from the fit of the measured Raman line profile vs. concentration (in mole fraction of acetone) plot.

upon dilution. This behavior is quite common and has been observed in other cases of isotope mixing studied earlier [18,27,33–35]. In most of the cases, the concentration dependence exhibits a linear behavior and this is what has been observed in the present case also. The upshift of  $\nu(\text{C}=\text{O})$  stretching upon dilution can be understood in terms of self-association. It is obvious from the optimized geometry of the dimer of  $(\text{CH}_3)_2\text{C}=\text{O}$  presented in Fig. 4(b) that a weak electrostatic link between the O atom of one  $(\text{CH}_3)_2\text{C}=\text{O}$  molecule and the H atom of the other  $(\text{CH}_3)_2\text{C}=\text{O}$  molecule is established. This electrostatic link known as hydrogen bond obviously withdraws some electronic charge density from the  $\text{C}=\text{O}$  region, thus reducing the force constant for the  $\nu(\text{C}=\text{O})$  stretch in the neat liquid, either acetone or acetone- $\text{d}_6$ . This is clearly seen in the ab initio calculations also. When the neat liquid is diluted by the isotopic species, chances of self-association as depicted in Fig. 4(b) are reduced to varying degrees depending upon the molar ratio of the two isotopic species. This, in effect, would increase the bond strength of  $\text{C}=\text{O}$  bond and hence the wavenumber of

the  $\nu(\text{C}=\text{O})$  stretching would be expected to increase upon dilution, as observed in this study (see Fig. 5).

The  $\text{C}=\text{O}$  bonds in  $(\text{CH}_3)_2\text{C}=\text{O}$  and  $(\text{CD}_3)_2\text{C}=\text{O}$  are alike and the wavenumber of  $\nu(\text{C}=\text{O})$  stretching may, therefore, be expected to show a similar concentration dependence. The  $\nu(\text{C}=\text{O})$  stretching shows a continuous upshift in the case of  $(\text{CD}_3)_2\text{C}=\text{O}$  and it also has a linear concentration dependence. The  $\nu(\text{C}=\text{O})$  stretching shows an upshift in the case of  $(\text{CH}_3)_2\text{C}=\text{O}$  also upon ID initially and has almost a linear dependence up to mole fraction of acetone  $x = 0.3$ . However, on further dilution, the  $\nu(\text{C}=\text{O})$  shows a trend of small downshift at  $x = 0.2$  which becomes much more pronounced and almost abrupt at  $x = 0.1$ . Since the  $\nu(\text{C}=\text{O})$  values are obtained from the fit, it was essential to examine that this downshift is not an artifact of Raman line shape analysis. The line shape analysis was performed repeatedly with several initial guesses, but it always led to a considerably low value of  $\nu(\text{C}=\text{O})$  stretching at  $x = 0.1$  consistently and we are led to believe that this downshift was a genuine effect. However, such an abrupt shift



and reversal of trend is not quite unlikely in isotopic mixtures and Kamogawa and Kitagawa [34] have observed both an abrupt change as well as reversal of trend in the isotopic mixture  $C_6H_6 + C_6D_6$  at high dilution where the wavenumber shifts were even much smaller ( $\sim 0.2 \text{ cm}^{-1}$ ) and were measured only by the RDS technique. Such an effect may be caused by the polarizability and volume differences between the parent and isotopic molecules as argued in that study [34].

### 5. Raman non-coincidence effect and its relationship with self-association

As pointed out earlier, the phenomenon of NCE in  $(CH_3)_2C=O$  has been studied repeatedly covering one aspect or the other [13,16–19,21–25]. The NCE arises basically due to short- and long-range orientational order arising from intermolecular and intramolecular interactions in dense polar liquids. The dipole moment of the molecule plays a vital role in creating this orientational order and hence, roughly speaking, the dipole moment of the molecule may be one of the major factors in deciding the magnitude of NCE and thereby the  $\Delta\nu_{nc}$  value defined in Eq. (1). The resonant transfer of energy from one oscillator to another in the neat liquid and reorientation order, the two main factors responsible for NCE, may have varying degree of influence on the  $\Delta\nu_{nc}$  value in isotopic mixtures with different molar ratios. An attempt was made in an earlier study [3] on the isotopic mixture  $CHBr_3 + CDBr_3$  to look for the influence of ID on the magnitude of  $\Delta\nu_{nc}$ . The totally symmetric  $\nu_1(C-H)$  mode of  $CHBr_3$  was selected for such a study. The following two expressions:

$$\Delta\nu_{nc} = -[I_0^R - I_2^R]\rho/(4\pi c\nu_G) \quad (4)$$

and

$$\Delta\nu_{ID} = -I_0^R\rho/(4\pi c\nu_G) \quad (5)$$

were given by Logan [1] for the NCE shift and ID shift, where  $\rho$  and  $\nu_G$  denote the number density in the neat liquid and vibrational wavenumber in the gas phase, respectively. The factors  $I_0^R$  and  $I_2^R$  represent the intervibrational coupling. If the orientational order in the neat liquid is negligible, one term  $I_2^R$  in Eq. (4)

vanishes and equal values of  $\Delta\nu_{nc}$  and  $\Delta\nu_{ID}$  are predicted. In the case of the isotopic mixture  $CHBr_3 + CDBr_3$  studied recently [3], the values of  $\Delta\nu_{nc}$  and  $\Delta\nu_{ID}$  were small and were determined precisely to be  $1.02$  and  $0.73 \text{ cm}^{-1}$ , respectively, and this observation was suggestive of the fact that short-range order is not negligible. In the present study on isotopic mixture  $(CH_3)_2C=O + (CD_3)_2C=O$  the values of  $\Delta\nu_{nc}$  and  $\Delta\nu_{ID}$  for  $\nu(C=O)$  of  $(CD_3)_2C=O$  are  $4.49$  and  $5.24 \text{ cm}^{-1}$ , respectively. These values were determined from the experimental data by fitting of the measured Raman line profiles and then extrapolating it to extreme dilution. Obviously these results suggest an influence of short-range order in the case of neat liquid. Since in the case of  $(CH_3)_2C=O$ , the  $\nu(C=O)$  shows an abrupt downshift at high dilution, a very accurate definition of  $\Delta\nu_{ID}$  is not available.

Another factor, that was examined in the earlier study [3] was the variation of  $\Delta\nu_{nc}$  with concentration in the isotopic mixture. It was very clearly seen in this study on  $CHBr_3 + CDBr_3$  that at a mole fraction of  $0.05$  of the reference molecule  $CHBr_3$ , the value of  $\Delta\nu_{nc} \rightarrow 0$ . An attempt was made to determine the  $\Delta\nu_{nc}$  variation for the  $\nu(C=O)$  vibration in the present study. Although it can be clearly seen from Fig. 2 that the value of  $\Delta\nu_{nc}$  decreases upon dilution, but due to close and even overlapping line profiles of the  $\nu(C=O)$  for the two isotopic molecules, a numerical estimate for  $\Delta\nu_{nc}$  at extreme dilution is not available. This is essentially because of the fact that the  $\nu(C=O)$  stretching vibrations for  $(CH_3)_2C=O$  and  $(CD_3)_2C=O$  are separated by only  $\sim 10 \text{ cm}^{-1}$ , whereas in the case of the isotopic mixture  $CHBr_3 + CDBr_3$ , the  $\nu(C-H)$  vibration was quite isolated, well separated from  $\nu(C-D)$  and its line profile could be precisely analyzed even at lower concentrations of  $CHBr_3$ . Furthermore, in the present study, at high dilution of  $(CD_3)_2C=O$ , the reduced degree of self-association would cause an upshift of the  $\nu(C=O)$  wavenumber for  $(CD_3)_2C=O$ , whereas the  $\nu(C=O)$  wavenumber for  $(CH_3)_2C=O$  would be nearly the same owing to its high concentration (in the highly diluted mixture for the reference system,  $(CD_3)_2C=O$ ). Thus the  $\nu(C=O)$  profiles for  $(CH_3)_2C=O$  and  $(CD_3)_2C=O$  come still closer making it practically impossible to have a reliable estimate of  $\Delta\nu_{nc}$  at high dilutions in the present study.

## 6. Concentration dependence of wavenumber shift and linewidth variation for totally symmetric $\nu_1(\text{C-H})$ mode of acetone

In view of the self-association and the ab initio calculations on the optimized geometry of

self-associated dimer, it was thought worth an exercise to look for the wavenumber shifts of the totally symmetric  $\nu_1(\text{C-H})/(\text{C-D})$  vibration of acetone/acetone- $\text{d}_6$ . The  $\nu_1(\text{C-H})$  was chosen for somewhat detailed study because this vibration was thoroughly investigated through time-resolved study

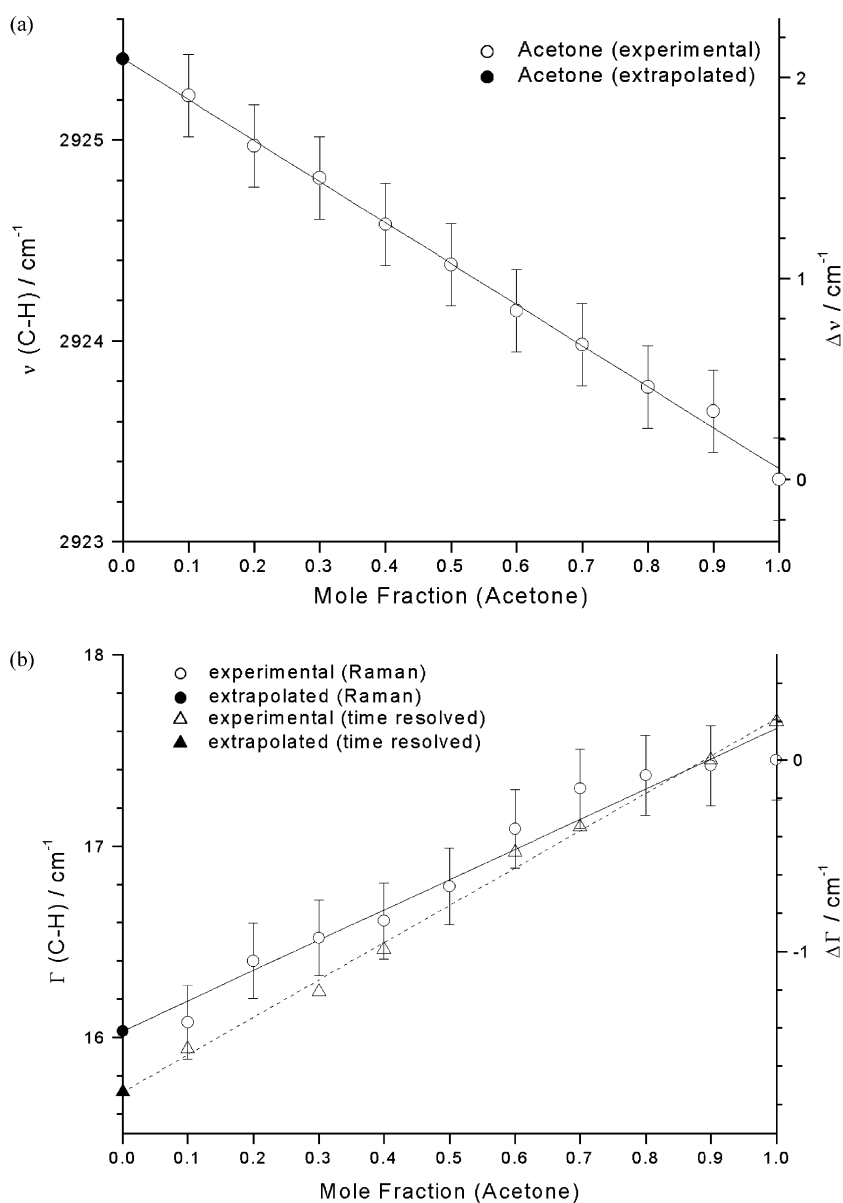


Fig. 6. (a) The wavenumber positions of  $\nu(\text{C-H})$  stretching vibration in acetone; (b) Linewidths  $\Gamma(\text{C-H})$  in acetone obtained from the experimental Raman data from the fit as in Fig. 5 and  $\Gamma(\text{C-H})$  as obtained from the dephasing rates determined in earlier time-resolved study [31], depicted as a function of concentration.

[31] and it was considered worthwhile to compare these results with our results, especially the line-width variation with concentration. A simultaneous study of wavenumber position, however, was also found interesting in view of self-association. As it is evident, whenever neat liquid  $(\text{CH}_3)_2\text{C}=\text{O}$  will be diluted with the isotopic species  $(\text{CD}_3)_2\text{C}=\text{O}$ , the degree of self-association would decrease and hence the wavenumber position of  $\nu_1(\text{C}-\text{H})$  would be expected to show an upshift. For neat  $(\text{CH}_3)_2\text{C}=\text{O}$ , the wavenumber position of  $\nu_1(\text{C}-\text{H})$  was obtained from the fit of the measured Raman line profile to be  $2923.32\text{ cm}^{-1}$  and it shows an upshift of  $2.04\text{ cm}^{-1}$  (extrapolated to  $x=0$ ; experimental accuracy is, however,  $\pm 0.1\text{ cm}^{-1}$ ) in going to infinite dilution as depicted in Fig. 4(a). Thus our experimental observations support what is expected due to self-association. A similar extrapolation was also made for the linewidths  $\Gamma(\text{C}-\text{H})$  obtained from the fit at different concentrations and the values were compared with the  $\Gamma(\text{C}-\text{H})$  values determined from  $T_2$  measured by Fickenschier et al. [31]. The results are presented graphically in Fig. 4(b). The  $\Gamma(\text{C}-\text{H})$  values obtained from the present study differ noticeably at higher dilution from those obtained from the study in time-domain [31]. This as well as some other related aspects are being addressed to in a rather detailed study [38].

## 7. Conclusions

The investigated  $\nu(\text{C}=\text{O})$  mode of  $(\text{CH}_3)_2\text{C}=\text{O}$  is one of the thoroughly investigated vibrations, but the number of studies in ID are only very scarce. A reliable data on wavenumber shift,  $\Delta\nu_{\text{nc}}$  caused by Raman NCE and  $\Delta\nu_{\text{ID}}$ , the shift in the wavenumber position at extreme dilution confirms the existence of a local short-range order in neat liquid, which is rather essential for the NCE to be exhibited. Apart from  $\nu(\text{C}=\text{O})$  stretching,  $\nu_1(\text{C}-\text{H})$  vibration was also studied as a function of concentration in isotopic mixtures with varying mole fraction. A comparison of the linewidth,  $\Gamma(\text{C}-\text{H})$  from the present study and those obtained from the dephasing study [31] in time-domain, especially at high dilution is presented (Fig. 6). The values of  $\Delta\Gamma(\text{C}-\text{H})$  as determined from fits are appreciably different; 1.58

(present study) and  $1.98\text{ cm}^{-1}$  (dephasing study, Ref. [31]). This may prove to be crucial result for testing the various theories of vibrational dephasing. The ab initio calculations provide a nice support to our experimental results. To the best of our knowledge, the present study is the first, where a synopsis of ID, Raman NCE, self-association supported by ab initio results is reported for an isotopic mixture.

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