

Evidence for Negative Cross Correlations in Vibrational Dephasing in Liquids: Isotropic Raman-Line Shift and Width Phenomena in Isotopic Mixtures of N₂ and O₂

Dietmar Keutel, Frank Seifert, and Karl-Ludwig Oehme*

Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany

Augustinus Asenbaum and Maurizio Musso†

Institut für Physik und Biophysik, Universität Salzburg, A-5020 Salzburg, Austria

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To experimentally confirm the hypothesis of negative cross terms between different dephasing mechanisms, potentially leading to a broadening of the isotropic Raman line upon isotopic dilution, we present a detailed study on the concentration dependencies of all of the line shifts and widths in the four isotopic mixtures of type $(^{15}\text{N}^{14}\text{N})_x-(^{14}\text{N}_2)_{1-x}$, $(^{15}\text{N}_2)_x-(^{14}\text{N}_2)_{1-x}$, $(^{15}\text{N}_2)_x-(^{15}\text{N}^{14}\text{N})_{1-x}$, and $(^{16}\text{O}_2)_x-(^{18}\text{O}_2)_{1-x}$ near the normal boiling point of nitrogen at $T = 77.35$ K. A quite disparate behavior of the nitrogen oscillators compared to the oxygen oscillators was observed in respect to a change of their isotopic baths.

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Although there is general agreement on the physics behind the principal dephasing (T_2) and depopulation (T_1) mechanisms leading to vibrational (nonrotational) line broadening in dense fluids (see [1] for early but nevertheless still valid reviews), the detailed identification of the different mechanisms which contribute to an individual line shape (LS) in a particular liquid remains an open task which necessitates, from an experimental point of view, very precise measurements in a wide range of thermodynamic states and, from a theoretical point of view, a precise modeling of fluid structure and dynamics. This work was inspired by the uncommon expectation that the *suppression* of an individual broadening process may *broaden* a given LS, as suggested by the pioneering molecular dynamics simulation of Oxtoby, Levesque, and Weis [2] and the following thorough theoretical analysis of Bratos and Tarjus [3] on the role of (intermolecular vibrational) resonance couplings (RC) on the dephasing mechanisms in vibrational LS in liquids.

The existence of various cross correlations $\langle x \cdot y(t) \rangle$ between different dynamic variables $x(t)$, $y(t)$ is one of the reasons why rationalization of vibrational LS becomes ambiguous in dense systems. Although the possible non-negligibility of cross phenomena was already discussed in the beginning of this field [4], any unambiguous experimental verification of its existence is still missing. The situation becomes especially cumbersome if the always present, (purely) environmentally induced, instantaneous frequency fluctuations $\Delta\omega_{\text{PD}}(t)$, i.e., the so-called “pure” dephasing (PD) [1], compete with contributions $\Delta\omega_{\text{RC}}(t)$ from RC between molecules. Then, vibrational LS’s are determined not only through both autocorrelation functions $\langle \Delta\omega_{\text{PD}} \cdot \Delta\omega_{\text{PD}}(t) \rangle$ and $\langle \Delta\omega_{\text{RC}} \cdot \Delta\omega_{\text{RC}}(t) \rangle$, but also through the respective cross correlation of type $\langle \Delta\omega_{\text{RC}} \cdot \Delta\omega_{\text{PD}}(t) \rangle$. By taking into consideration that any autocorrelation is characterized by a zero time average which is positive *per se*, whereas the sign of the cross effect $\langle \Delta\omega_{\text{RC}} \Delta\omega_{\text{PD}} \rangle$ cannot be determined from first

principles, it becomes imaginable that a negative cross correlation may overcompensate the autocorrelation due to RC. Therefore, the *switch off* of vibrational RC *might broaden* a given LS rather than narrow it, the latter being usually expected and commonly observed when decoupling oscillators [5]. The simulation [2] indicated the relevance of this type of broadening in liquids: the isotropic Raman LS of liquid nitrogen should *broaden* (by up to about 10%) with gradual *switch off* of RC with *increasing* isotopic dilution (ID). From a formal point of view, this situation became clear in detail with Ref. [3], resulting in the following mole fraction (x) dependence of the isotropic LS $J_{\text{iso}}(\omega, x)$ (valid within the second cumulant approximation [1]):

$$J_{\text{iso}}(\omega, x) = \text{FT}\{\exp[i(s_1 + s_2x)t - w_{11}(t) + (2w_{12}(t) + w_{22}(t))x + w_{23}(t)x^2]\}. \quad (1)$$

Here FT represents a Fourier transform, and the imaginary part describes the linear line shift $\omega_0(x)$ with intercept s_1 and slope s_2 , the latter characterizing the ensemble averaged shift which is induced by RC. The real term in brackets in Eq. (1) describes the line broadening, where the two $w_{jj}(t) > 0$ are autocorrelations of either $\Delta\omega_{\text{PD}}(t)$ ($j = 1$) or $\Delta\omega_{\text{RC}}(t)$ ($j = 2$) and the two $w_{jk}(t)_{j \neq k} \geq 0$ are responsible for the cross effects. $w_{12}(t)$ describes the correlation between $\Delta\omega_{\text{PD}}(t)$ and $\Delta\omega_{\text{RC}}(t)$, and $w_{23}(t)$ characterizes the (excitonlike) three particle RC; see Ref. [3] for a more detailed discussion and Ref. [6] for an experimental verification of this theory. As long as an (ideal) ID is considered, there is no hidden x dependence in the s_i and the $w_{jk}(t)$ above, whereas any chemical dilution will change these ensemble averages in an as yet unpredictable way. Generally, using ID as the sole method to isolate the influence of RC among the T_2 processes demands two idealizations which are hard to fulfill experimentally: (i) The isotopic mixture of species A and B

should be as ideal (in the thermodynamic sense) as possible, that means that the interaction potentials A - A , A - B , and B - B should be congruent, i.e., second order changes of structure and dynamics should be minimized. (ii) Nearly resonant intermolecular energy transfer between A (vibrational frequency $\omega_0^{(A)}$) and B ($\omega_0^{(B)}$) should be avoided, i.e., $\hbar|\omega_0^{(A)} - \omega_0^{(B)}| \gg k_B T$, meaning that any intermolecular T_1 channel, if present, should stay constant upon change of the isotopic environment. The first point is questionable for the usual ID experiments with H/D substituted (small) molecules, especially, but not only, in hydrogen-bonded liquids, whereas the second point becomes important with increasing density of vibrational states which may catalyze T_1 processes down to the picosecond time scale and/or with increasing reduced mass of the oscillator, especially if the linewidth increases up to the magnitude of $|\omega_0^{(A)} - \omega_0^{(B)}|$.

N_2 as the prototype of the harmonic diatomic oscillators, and therefore weakly coupled to the bath, fulfills the above mentioned criteria unmatched and therefore becomes best suited for this type of LS analysis (see Ref. [7] for the early work). However, the extremely narrow linewidth [$0.058(2) \text{ cm}^{-1}$ near its normal boiling point [8]] and the cryogenic nature of the liquid prevented up to now any detailed ID studies, despite their obvious relevance [9]. Therefore, up to now, no one verified experimentally the statement in Ref. [2], apart from a hint in Ref. [10]. A detailed determination of the concentration dependencies of linewidth $fwhm(x)$ and position $\omega_0(x)$ is needed in order to obtain an unequivocal answer to (i) whether the LS of liquid N_2 is significantly affected by RC (it is usually interpreted by postulating its negligibility [11]) and, if so, (ii) to confirm the concept of negative cross correlations. To realize this, we studied each of the isotopomeric species in the three (orthobaric) nitrogen mixtures $(^{15}N^{14}N)_x-(^{14}N_2)_{1-x}$, $(^{15}N_2)_x-(^{14}N_2)_{1-x}$, $(^{15}N_2)_x-(^{15}N^{14}N)_{1-x}$, and, for comparison, the oxygen mixture $(^{16}O_2)_x-[(^{18}O_2)_{0.92}/(^{16}O^{18}O)_{0.08}]_{1-x}$.

The “neat” samples of $^{15}N_2$ (98% ^{15}N) and $^{18}O_2$ (96.26% ^{18}O , 3.74% ^{16}O) were purchased from CHEMOTRADE GmbH, Leipzig. $^{14}N^{15}N$ was synthesized via diazotization of $^{15}NH_4Cl$ (99% ^{15}N) and purified using standard techniques. Unfortunately, $^{16}O^{18}O$ could not be varied in the whole x range, because we did not find any simple synthesis of it. The gaseous samples were mixed within ± 0.005 units of x using standard volumetric techniques, transferred into narrow glass tubes with polished bottoms, and finally sealed. They were immersed—using a home-made all-glass dewar—in a liquid-nitrogen cooling bath, boiling at $77.2(2) \text{ K}$ (including the fluctuations of the ambient pressure during a period of eight months). The scattering setup is a standard one (90° geometry, etalon equipped Lexel Model 95 Ar^+ laser tuned to 514.5319 nm in single-mode, coaxial guidance of the beam of approximately 300 mW within the sample

tube). To detect the Raman light, we used a double monochromator (SOPRA DMDP 2000, $f = 2 \text{ m}$, single pass) equipped with a charge-coupled-device (CCD) camera. In order to obtain an adequate signal-to-noise ratio, up to 15 spectra for each x with integration times up to 5 min were collected. To determine $\omega_0^{(i)}(x_i)$ —taking into account the thermal drift of the spectrometer—three supplementary spectra were taken with additional light from different noble gas spectral lamps (Oriel PenRay). Since the Raman light from our samples is strongly polarized and the anisotropic contribution is broader by at least 3 orders of magnitude, the $J_{iso}(\omega)$ are approximated by the parallel spectra $J_{||}(\omega)$. The true LS’s were approximated according to $1/J(\omega) \propto \sum_{n=0}^4 a_n(\omega - \omega_0)^n$, as justified by the Lorentzian nature of $J(\omega)$ [8], convoluted with the Gaussian instrumental function ($fwhm = 0.055 \text{ cm}^{-1}$), and fitted to the experimental LS. See Fig. 1 to judge the quality of our spectra and to get an idea of the magnitude of dilution-induced shift.

Our results are summarized in Figs. 2 and 3. At first glance, the strictly linear concentration dependencies $\omega_0^{(i)}(x_i) = s_1 + s_2 x_i$ [see Eq. (1)] confirm the existence of the RC effect and its formal interpretation in the language of Ref. [3]. However, it becomes evident that the $J_{iso}(\omega)$ of N_2 and O_2 shows quite disparate x dependencies upon ID: The six infinitely diluted states of N_2 were uniformly shifted by $+183.2(11) \text{ ppm}$ relative to the band center of the respective neat liquids, while for O_2 this value was $-87.2(9) \text{ ppm}$. It is important to note that these relative shifts are invariant against the change of the isotopic oscillator and its isotopic environment. The scaled gas-to-liquid shift [which documents the internal consistency of our measurements (see the last column in Table I)] demonstrates that intermolecular interactions are

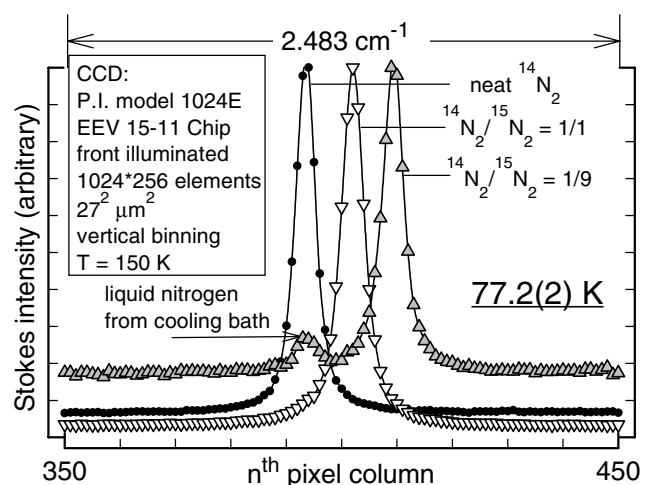


FIG. 1. Examples of experimental $^{14}N_2$ CCD spectra near 584.522 nm : The “1/9” curve gives an example of the magnitude of the shift, when sampling light from the diluted $^{14}N_2$ (in $^{15}N_2$) probe and the undiluted $^{14}N_2$ from the cooling bath.

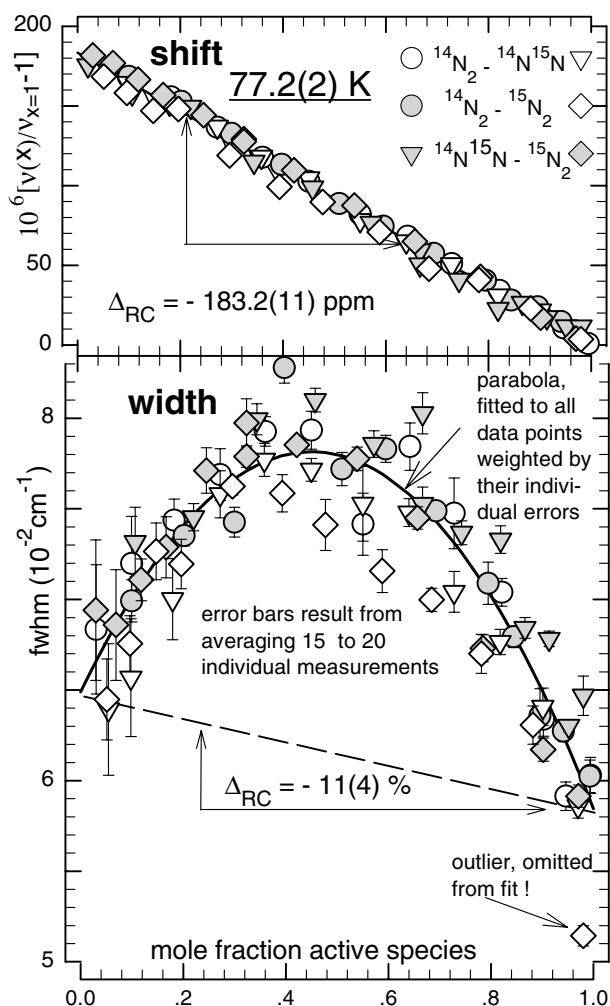


FIG. 2. N_2 : Concentration dependencies of line shift (top) and (full) line width (at half-height) (bottom). Note that the shifts are scaled according to $\nu_{0,i}(x_i)/\nu_{0,i}(x_i = 1) - 1$. The solid line gives a polynomial up to the second order in x (fitting all data points) [see the real part of Eq. (1)].

weaker in N_2 than in O_2 . The latter, to our knowledge, represents the only example where ID results in a lowering of ω_0 , showing the sensitivity of RC on the finer details of the interplay of the intermolecular interaction with the intramolecular vibrational potential. In this sense it seems to be of importance to reconsider two early works treating the solvent-induced shifts of N_2 [8] and CO [12] in various cryogenic liquids near 78 K: Both ω_{N_2} and ω_{CO} increase (by about 100 and 230 ppm, respectively) upon dilution of the active species in the “pseudoisotopic” mixture $(N_2)_x(CO)_{1-x}$ of two isoelectronic components. However, if the more chemical systems $(CO)_x(O_2)_{1-x}$ [12] and $(N_2)_x(O_2)_{1-x}$ [8] are considered, ω_{CO} and ω_{O_2} decrease by about 260 and 240 ppm, respectively. Thus, it seems to be that the abnormal behavior of the O_2 frequencies in our isotopic mixture is more likely governed by the intermolecular interaction than by the intramolecular vibrational potential.

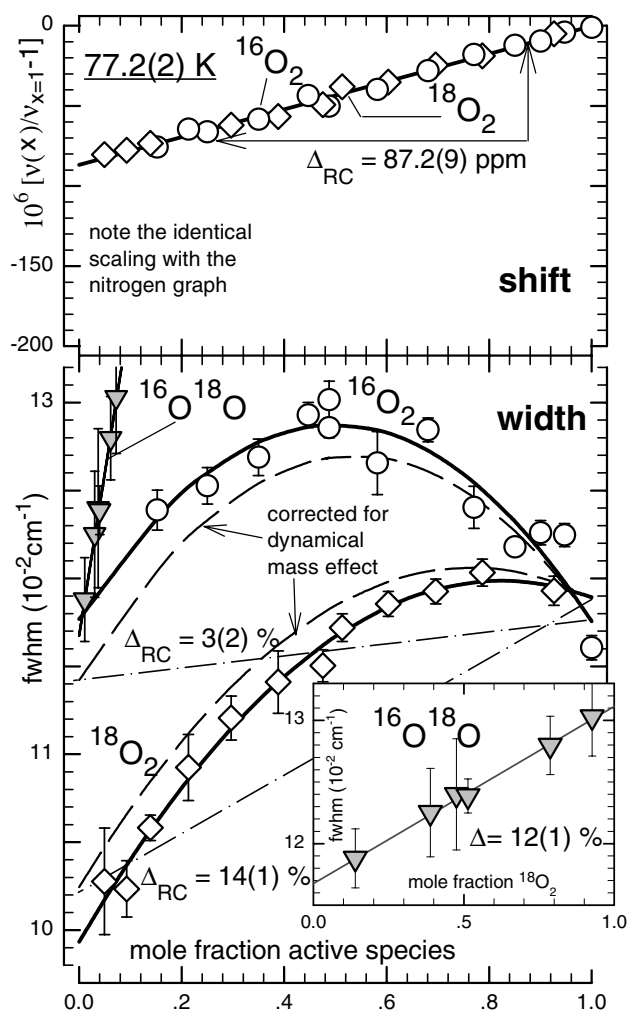


FIG. 3. O_2 : Concentration dependencies of line shift (top) and line width (bottom). The broken lines give the corrections to the dynamical mass effect following the “isolated binary collision” model (see [1]). The bottom inset gives the width of the $^{16}O^{18}O$ species as a function of $^{18}O_2$ fraction. Note that totally $0 < x(^{16}O^{18}O) \leq 0.076$. See Fig. 2 for further explanations.

The most evident characteristics of the functions $fwhm(x_i)$ is their parabolic appearance, due to environmental fluctuations which are at maximum for the equimolar mixture. The extent of nonlinearity is larger in N_2 than in O_2 , corresponding with the fact that the nonlinearity correlates with the magnitude of the solvent-induced shift ($d\omega_o^{(i)}/dx_i$), by which the parabolic $fwhm(x_i)$ can be well reproduced with the Bratos-Tarjus formalism [3] in its fast modulation limit. Considering the concentration behavior of the six N_2 states (Fig. 2) no variation between the different isotopic species can be found within the experimental error. One might argue, keeping in mind the well-known dephasing models, that both an intermolecular and an intramolecular $^{15}N/^{14}N$ mass effect should be detectable [1], i.e., there should be a difference if we consider the “light” oscillator $^{14}N_2$ in the “heavy” solvent $^{15}N_2$ or vice versa. Furthermore, as mentioned above, a

TABLE I. The gas-to-liquid shifts of the isotopic species. The isolated molecule frequency of $^{18}\text{O}_2$ has been harmonically extrapolated from the correspondig value of $^{16}\text{O}_2$ [14].

Species	$\nu_{0-1}^{J,J'=0a}$ (cm^{-1})	$\nu_{\text{max}}^{(i)}(x_i = 1)^b$ (cm^{-1})	$\nu_{0-1}^{J,J'=0} - \nu_{\text{max}}^{(i)}$ $10^{-3} * \nu_{0-1}^{J,J'=0}$
$^{14}\text{N}_2$	2329.92(1)	2326.55(1) ^c	1.45(1)
$^{14}\text{N}^{15}\text{N}$	2291.33(1)	2287.96(1)	1.47(2)
$^{15}\text{N}_2$	2252.125(15)	2248.71(1)	1.51(2)
$^{16}\text{O}_2$	1556.379	1551.64(1)	3.05(1)
$^{18}\text{O}_2$	[1468.652] _h	1464.17(1)	[3.06]

^a $\nu_{0-1}^{J,J'=0}$, see [15].

^bIncludes $\Delta_{\text{vacuum}} = -0.6385(\text{N}_2), -0.4181(\text{O}_2) \text{ cm}^{-1}$.

^cFor comparison: $\nu_0(78 \text{ K})_{x=1} = 2326.534 \text{ cm}^{-1}$ [16] and $\nu_0(77.4 \text{ K})_{x=1} = 2326.5133 \text{ cm}^{-1}$ [17].

lower lying state catalyzes the higher lying one more efficiently than the higher state catalyzes the lower one, i.e., $^{14}\text{N}^{15}\text{N}$ should be more effective in the depopulation of $^{14}\text{N}_2$ than vice versa, the Boltzmann factor being the reason for this asymmetry [13]. Fortunately, both phenomena are well within the experimental error. Therefore, the fact that *all* six diluted states of N_2 oscillators are *broader* than their corresponding three neat states strongly supports the idea that negative cross correlation terms overcompensate the positive RC autocorrelation term. By weighting all of the 73 data points according to their error bars only, we obtained a 11(4)% broadening going from the neat to the infinitely diluted state. This confirms the simulation in Ref. [2], even quantitatively.

The catalysis of the depopulation of the lighter oscillator by a heavier one becomes evident in the O_2 liquid, where the linewidth of the spurious $^{16}\text{O}^{18}\text{O}$ strongly depends on the $^{16}\text{O}_2/^{18}\text{O}_2$ ratio in its environment (see the inset in Fig. 3), i.e., the $^{18}\text{O}_2$ level, lying lower by 44.38 cm^{-1} , is more effective in catalyzing the $^{16}\text{O}^{18}\text{O}$ depopulation than the $^{16}\text{O}_2$ level lying higher by 43.09 cm^{-1} . The above-mentioned dynamical mass effect alone (the broken lines in the lower part of Fig. 3) cannot be made responsible for the significant difference observed in the two dilution curves. Therefore, the $^{18}\text{O}_2$ curve, which shows the usual ID behavior contrary to the unusual behavior of N_2 , is more representative for RC than the $^{16}\text{O}_2$ curve.

In conclusion, we have experimentally confirmed the relevance of negative cross correlations in line broadening processes, since line broadening observed upon isotopic dilution in *all* of the $^{14}\text{N}/^{15}\text{N}$ isotopically modified nitrogens allows this sole interpretation, the quite opposite behavior of the oxygens showing the extreme sensitivity to the details of the intermolecular potential.

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*Email address: Karl-Ludwig.Oehme@rz.uni-jena.de

†Email address: Maurizio.Musso@sbg.ac.at

- [1] D. W. Oxtoby, Adv. Chem. Phys. **40**, 1 (1979); **47**, 487 (1981); W. G. Rothschild, *Dynamics of Molecular Liquids* (Wiley, New York, 1984).
- [2] D. W. Oxtoby, D. Levesque, and J.-J. Weis, J. Chem. Phys. **68**, 5528 (1978); D. Levesque, J.-J. Weis, and D. W. Oxtoby, J. Chem. Phys. **72**, 2744 (1980).
- [3] S. Bratos and G. Tarjus, Phys. Rev. A **32**, 2431 (1985); see also D. E. Logan, Mol. Phys. **58**, 97 (1986).
- [4] R.-M. Lynden-Bell, Mol. Phys. **33**, 907 (1977); R. K. Wertheimer, Mol. Phys. **36**, 1631 (1978).
- [5] G. Döge, Z. Naturforsch. **28A**, 919 (1973).
- [6] K.-L. Oehme and K. Klostermann, J. Chem. Phys. **89**, 2124 (1989).
- [7] M. J. Clouter, H. Kiefte, and C. G. Deacon, Phys. Rev. A **33**, 2749 (1986), and references therein.
- [8] S. A. Akhmanov, F. N. Gadjiev, N. I. Koroteev, R. Yu. Orlov, and I. L. Shumay, Appl. Opt. **19**, 859 (1980). By using CW coherent anti-Stokes Raman Spectroscopy with its large dynamical range, it has been shown that $J(\omega)$ of neat N_2 near 78 K is strictly Lorentzian in the range $10^{-4} \lesssim J(\omega)/J(\omega_0) \lesssim 1$.
- [9] H. J. van Elburg and J. D. W. van Voorst, Chem. Phys. **113**, 463 (1987); H. M. M. Hesp, J. Langelaar, D. Bebelaar, and J. D. W. van Voorst, Phys. Rev. Lett. **39**, 1376 (1977).
- [10] J. De Kinder, E. Goovaerts, A. Bouwen, and D. Schoemaker, Phys. Rev. B **42**, 5953 (1990); J. De Kinder, A. Bouwen, and D. Schoemaker, Chem. Phys. Lett. **203**, 12 (1993). Considering a diluted mixture of $^{15}\text{N}_2$ in $^{14}\text{N}_2$ just above the $36.5 \text{ K } \beta \rightarrow \alpha$ transition, the observation of a broader line of the minor component $^{15}\text{N}_2$ compared to the major component $^{14}\text{N}_2$ gives some hint concerning the existence of RC, not only in the disordered solid but also in the liquid.
- [11] M. I. M. Scheerboom, J. P. J. Michels, and J. A. Schouten, J. Chem. Phys. **104**, 9388 (1996).
- [12] S. R. J. Brueck, Chem. Phys. Lett. **53**, 273 (1978).
- [13] M. M. Matti, E. A. Gregory, and C. J. S. M. Simpson, Chem. Phys. **95**, 43 (1985).
- [14] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* Molecular Spectra and Molecular Structure Vol. IV (Van Nostrand, New York, 1979).
- [15] J. Bendtsen, J. Raman Spectrosc. **2**, 133 (1974).
- [16] B. Oksengorn, D. Fabre, B. Lavorel, R. Saint-Loup, and H. Berger, J. Chem. Phys. **94**, 1774 (1991).
- [17] R. D. Beck, M. F. Hineman, and J. W. Nibler, J. Chem. Phys. **92**, 7068 (1990).