Raman line shape studies of hydrogen cryosolutions

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Abstract. The pure rotational and rotation-vibration Raman transitions in H₂ dissolved in liquid argon (LAr, T=87 K) and nitrogen (LN₂, T=80 K) are studied at different hydrogen concentrations. Whereas the rotational S₀(J) (J=0, 1) shapes of H₂-LAr can be accurately fitted by Lorentzian profiles, the wings of the same H₂-LN₂ lines demonstrate a distinct sub-Lorentzian behaviour. The difference between these patterns is attributed to the change of the time scale of anisotropic interactions which perturb the rotational motion of H₂. They should be slower for the H₂-LN₂ system in which the long-range quadrupole-quadrupole interactions develop. The latter dominate in the formation of the symmetric H₂-LN₂ S₁(J) line shapes. By contrast, the same H₂-LAr lines are mainly monitored by the vibrational broadening and their shapes are distinctly asymmetric.

1. Introduction
Hydrogen molecule, H₂, and its isotopic substituents are unique molecular objects which pertain almost unhindered quantized rotation even in condensed phases. Their line shapes contain a wealth of state-resolved information on couplings of molecular degrees of freedom with the bath and can therefore shed light on the microdynamics of liquids. Intriguing line asymmetry in the roto-vibrational Raman spectra of hydrogen in liquid SF₆ has been observed [1,2], while the rotational lines remained symmetric [1,3]. In other reference cryosolvents (LAr, LN₂), the asymmetry remained undetectable whatsoever [2,3]. However, the latter result may be doubted because of the insufficient Signal-to-Noise (S/N) ratios attained in the earlier studies. Generally, the existing data on the line profiles in the considered spectra are poor, semi-quantitative and lacking systematic treatment. To clarify the issue, the Raman line shapes of H₂ dissolved in liquid argon and nitrogen are now revisited with the use of the state-of-the-art spectroscopic techniques.

2. Experimental
The conventional 90°-detection experimental setup exploiting the triple Princeton Instruments TriVista TR557 spectrometer was employed. The native perpendicular to the scattering plane polarization of the Ar⁺ laser light source (514.5 nm) was not varied since the recorded transitions are known to be totally depolarized. The spectral resolution reached the value of 0.2 cm⁻¹, sufficient to avoid the slit distortions of the studied profiles. The S/N ratios were 1-2 decimal orders better than attained in older experiments [1-3]. The Raman setup was equipped with liquid-nitrogen cryostat that allows measuring the spectra at low temperatures with stability better than 1 K.
3. Results
The rotational $S_0(J)$ and roto-vibrational $S_1(J)$ lines ($J=0, 1$) of hydrogen were studied in LAr ($T=87$ K) and LN$_2$ ($T=80$ K). In order to trace the concentration effects on the line profiles, the hydrogen concentration $x$ was varied in the range 0.02-0.08 mole fractions. However, we were unable to observe any effect in both cryosystems, in contrast to the earlier reported slight self-broadening of the $S_0(J)$ lines in LN$_2$ [3]. We emphasize that the $S_0(J)$ shapes of H$_2$-LAr at detunings $\pm |z|$ from the line centers accessible for the investigation ($|z| \leq 20$ cm$^{-1}$) are found to strictly follow the Lorentzian distribution corrected by the quantum asymmetry factor $Q(z) = 2/[1 + \exp(\hbar z/kT)]$ (see figure 1).

The appearance of a Lorentzian shape is remarkable, for it is an indication of the fast varying molecule-bath interaction [4].

![Figure 1. Measured rotational Raman line shape of H$_2$-LAr cryosystem (dots) fitted by Lorentzian function (solid line).](image)

Generally, the memory function theory [4] predicts the isolated-line intensity to vary as $I(z) \sim \text{Re}[iz + \Gamma(z)]^{-1}$, where $\Gamma(z)$ is the one-sided Fourier transform of the time autocorrelation function characterizing the molecule-bath interactions. At detunings satisfying $zt_c << 1$ (where $t_c$ characterizes the decay rate of the interaction correlation function), one has $\Gamma(z) \approx \Gamma(0)$ and the line shape becomes Lorentzian. If, additionally, $\Gamma(0)t_c << 1$ (impact limit), the dispersion intensity distribution applies not only to the central part of the line but also to its near wings. At even larger detunings, $\Gamma(z)$ damps out and the intensity distribution in the wing becomes sub-Lorentzian, $I(z) \sim \text{Re} \Gamma(z)/z^2$. In this range, $F(z) = I(z)z^2$ decreases with $z$, as is evident from figure 2 where the symmetrized functions $\tilde{F}(z^*) = F(z)/Q(z)$ are plotted for the $S_0(1)$ line for both cryosolutions.

To visualize the different dynamical properties of two cryosystems, the dimensionless frequencies $z^* = z/\Gamma$ were used, with the half widths $\Gamma = \text{Re} \Gamma(0)$ found (see table 1) by the least-square fitting of the experimental profiles by the extended (quantum-corrected) Lorentzians. The different behavior of the line wings on figure 2 is striking. While no regular deviations from the extended Lorentzian distribution are observable for H$_2$-LAr, which confirms the impact character of the anisotropic H$_2$-Ar interactions, $\Gamma(z)$ for the nitrogen solution begins to decrease as the detuning exceeds three half widths. For the latter case, rough estimation gives the effective half width of the Re$\Gamma(z)$ spectrum to be about 40 cm$^{-1}$. If one assumes that the quadrupole-quadrupole H$_2$-N$_2$ interactions dominate and that their spectrum is formed mainly by the hindered rotation of N$_2$, then the width of Re$\Gamma(z)$ can be independently estimated from the collision-induced absorption by liquid nitrogen [5]. The resulting
value based on such IR data is 40-50 cm\(^{-1}\), in close agreement with our result, which can serve as an indication of the rotational coupling nature of the H\(_2\)-LN\(_2\) solution. The H\(_2\)-LAr interactions are shorter-ranged than the H\(_2\)-LN\(_2\) ones and, due to this, produce the \(\Gamma(z)\) spectrum so broad that its decay can not be spectroscopically traced.

**Figure 2.** Example of experimental distributions for rotational \(S_0(J)\) lines as functions of dimensionless detuning \(z^*\) for H\(_2\)-LAr (\(S_0(0)\) line, filled squares) and H\(_2\)-LN\(_2\) (\(S_0(1)\) line, open circles) solutions. \(\Gamma\) values were found by Lorentzian fits.

Analysis of the rotation-vibration line shapes also led to interesting results. Strikingly, the \(S_1(J)\) \((J=0,1)\) shapes of H\(_2\)-LAr regularly deviate from the extended Lorentzian profiles at lower frequencies, but not at higher ones, as seen on figure 3. In contrast to this, similar deviations detected in the H\(_2\)-LN\(_2\) \(S_1(J)\) profiles are symmetric and resemble those observed in the rotational spectrum of this system.

Data from table 1 allow to conclude that the vibrational contributions dominate in the roto-vibrational line broadening in the H\(_2\)-LAr system. Besides, preliminary data on the \(Q_1(J)\) line shapes show that, in contrast to the results on the pure rotational shapes of this cryosystem, the simulated Lorentzian \(Q_1(J)\) wings are somewhat higher than the observed ones. Since the \(Q_1(J)\) lines are solely broadened by the vibrational molecule-bath interactions, this can indicate on the slower evolution of the vibrational interactions in comparison to the anisotropic ones which relax in this system almost instantaneously.

**Table 1.** Measured shifts (\(\delta\)) and half widths (\(\Gamma\)) of the \(S_0(J)\) and \(S_1(J)\) Raman lines \((J=0,1)\) of hydrogen in cryosolutions. Units are wavenumbers, cm\(^{-1}\). Transition frequencies of free molecule were taken from Ref. [5].

| Transition | \(H_2\) in liquid argon, \(T=87\) K | \(H_2\) in liquid nitrogen, \(T=80\) K |
|------------|---------------------------------|---------------------------------|
| \(S_0(0)\) | \(-0.8\)                         | \(2.5\)                         |
| \(S_0(1)\) | \(-1.1\)                         | \(0.5\)                         |
| \(S_1(0)\) | \(-9.6\)                         | \(-7.3\)                        |
| \(S_1(1)\) | \(-8.5\)                         | \(-3.8\)                        |
Also, table 1 shows that the vibrational contributions to the H$_2$-LN$_2$ roto-vibrational line widths are three times smaller than the rotational ones. The balance in this case is thus in favor of the rotational broadening.

Considering the aforementioned facts altogether, we may suggest that the asymmetry of the roto-vibrational lines in the H$_2$-LAr cryosolution is an effect of the pronounced non-impact vibrational relaxation accompanied by a fast decorrelation of anisotropic molecule-bath interactions.

4. Conclusion
As found by the present study, the shapes of the rotational and roto-vibrational Raman lines of hydrogen dissolved in liquid argon and nitrogen are nearly Lorentzian. To interpret the observed deviations from the dispersion profiles, the vibrational and rotational couplings of H$_2$ with the bath are to be characterized by finite time scales. Depending on the relative roles of these couplings as well as on their characteristic times, the deviations can show up in the roto-vibrational line asymmetry as was indeed detected for the H$_2$-LAr cryosolution.

References
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