

7-1979

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Recommended Citation

S. L. Whittenburg and C. H. Wang. 1971. Comment on "Depolarized Rayleigh spectroscopy from benzonitrile". *Journal of Chemical Physics* 71 (1): 561-562.

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research was supported in part by the Scientific Research Fund of the Japanese Ministry of Education, Grant No. 364143.

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COMMENTS

Comment on "Depolarized Rayleigh spectroscopy from benzonitrile"

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(Received 20 September 1978; accepted 4 April 1979)

In their recent article Alms and Patterson¹ reported that the translation-rotation coupling parameter in benzonitrile is temperature independent. This is in contradiction to the results of our earlier study.² This discrepancy has been attributed to the effect of convolution of the true spectra with the instrumental spectrum. In this comment we report the effect of deconvolution on the translation-rotation coupling parameter as measured by depolarized Rayleigh light scattering.

For 90° scattering a convenient method for calculating the experimental spectrum is to convolute⁴ Eq. (1) of Ref. 2 with the measured instrumental spectrum and vary the unknown parameters Γ , the linewidth and R , the translation-rotation coupling parameter, until the best fit of the calculated spectrum to the experimental spectrum is attained. Due to experimental difficulties two additional parameters, a baseline and an amplitude factor, must also be included as well as a correction

for overlapping adjacent orders. A less satisfactory method is to allow the ratio $q^2\eta/\rho$ to be an adjustable parameter, as was done in Ref. 1 for the reason that these quantities can be measured for benzonitrile accurately. Therefore, even though the fitting procedure used in Ref. 1 mimics the effect of convolution we have some reservation about their final values of the coupling parameter. Given in Table are our values of R and $q^2\eta/\rho$ using our convolution method with only Γ and R as adjustable parameters. As a check, the best values of R and $q^2\eta/\rho$ allowing Γ , R and $q^2\eta/\rho$ as parameters are also given. One notes that while the true $q^2\eta/\rho$ values are consistently smaller than the light scattering values, the difference has a small effect on R . Also given in Table I are the values reported by Alms and Patterson. The differences in the magnitudes of $q^2\eta/\rho$ arise because Alms and Patterson used incident light at 5145 Å while our measurements were made using the 4880 Å line. As seen in Table I the decrease in R with increasing

TABLE I. Translation-rotation coupling parameter and measured and fit values of $q^2\eta/\rho$. $q^2\eta/\rho$ is in GHz. Also given is the sumsquare of residuals of the least squares fit.

$T(K)$	$q^2\eta/\rho$ (direct)	R	$q^2\eta/\rho$ (l. s.)	R	χ^2	$q^2\eta/\rho^a$ (direct)	$q^2\eta/\rho^a$ (direct)	R^a
263	0.291	0.38 ± 0.04	0.309	0.37	1.30	0.276	0.330	0.35
273	0.231	0.37 ± 0.03	0.261	0.35	0.38	0.218	0.232	0.36
283	0.194	0.32 ± 0.03	0.210	0.32	0.60	0.179	0.211	0.38
293	0.165	0.28 ± 0.03	0.169	0.28	0.58	0.152	0.121	0.37

^aReference 1.

temperature is greater than the error in the measurement.

The free spectral range (FSR) of 13.26 GHz used by Alms and Patterson is smaller than our choice of 32 GHz. While the smaller FSR gives more data points in the dip region it gives a much larger overlap of adjacent spectral orders. The fitting routine must then fit to numerous adjacent orders plus a floating baseline. This greatly increases the error in value obtained the Γ and therefore in the coupling parameter R . Thus, the slightly smaller free spectral range used in Ref. 1 does not constitute an advantage.

Alms and Patterson also find pair correlation to be important in benzonitrile, in contradiction to our result. Since Alms and Patterson did not do a concentration-dependent study they argued for the existence of pair correlation based on a slip boundary condition model. Although the slip model is applicable for most small molecular liquids our results have shown that it is not acceptable for benzonitrile. While in benzonitrile, one expects contributions of the depolarized scattering intensity to arise from orientation about the three principal axes, the dominant contribution in the depolarized intensity will be due to the orientation of the CN bond associated with the slowest molecular axis. Thus, instead of using the general formula employed in Ref. 1, it is important to weigh more heavily the contribution from the rotation of the slowest molecular rotation axis when estimating the reorientation rate using the Stokes-Einstein's formula. Assuming the depolarized Rayleigh spectral intensity is due to the reorientation of the slow axis, we have found in benzonitrile, as in nitrobenzene,⁵ the stick model more accurately describes molecular orientation. Our estimated value differs from that of Ref. 1 by a factor of 2, due mainly to the emphasis of the reorientation of the slowest molecular axis. Furthermore, our determination of the pair correlation factor from a concentration dependent depolarized Rayleigh study is more reliable than the total intensity measurement which requires corrections such as index of refraction and local fields.

They also argue that hydrogen bonding between benzonitrile and the tertbutyl alcohol solvent may lead to our result that $f=0$ in benzonitrile.⁶ We have shown, however, that for the pyridine- CCl_4 ⁷ and pyridine-cyclohexane⁸ systems that complex formation between solute and solvent does not influence the measurement of the static pair correlation factor. In the case of the pyridine- H_2O system, hydrogen bonding tends to increase the pair correlation and not to decrease it.⁹ Thus it is unlikely that hydrogen bonding between benzonitrile and tertbutyl alcohol can make $\Gamma\eta$ to become independent of benzonitrile concentration. However, experimental studies

of the reorientation time of benzonitrile in different optically isotropic solvents may lead to a better clarification.

We conclude that our previously reported values of the translation-rotation coupling parameter R in benzonitrile at high temperatures are small due to the neglect of deconvolution of the instrumental linewidth. With proper deconvolutions we have found that R still decreases with increasing temperature, in contradiction to the results reported by Alms and Patterson. It should be noted that the error in the value of R is large. One may then argue that our values of R agree with Alms and Patterson's values at the three lowest temperatures with the experimental error, but the disagreement at the highest temperature is outside the error bar. The decrease in R with increasing temperature is also larger than the range in the error.

In a recent paper by Wang,¹⁰ it is shown theoretically that the dynamic rotation-translation coupling is necessarily temperature dependent. At low temperature, due to the decrease in anharmonicity in the intermolecular force, the coupling constant is expected to decrease. At high temperature, on the other hand, rapid molecular motion is expected to decrease the coupling constant as well. Thus one expects a maximum in the coupling constant at some temperature. The observation of the maximum is however not yet reported.

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