PHASE-INDEPENDENT RATIO PARAMETERS FOR SATURATION TRANSFER EPR

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ABSTRACT Molecular dynamics have been studied by saturation transfer EPR. Rotational correlation times are obtained from the quadrature signal, as a ratio of spectral intensities at different field positions. It is possible to define ratio parameters that are independent of the phase of the modulation, but that can reduce to ratio parameters previously defined.

Saturation transfer EPR signals are routinely obtained using the quadrature-detected absorption signal at the second harmonic of the field modulation. Information on the molecular dynamics is obtained from ratio parameters of signal intensities at two different field values as originally defined by Thomas et al. (1). We shall refer to these parameters as TDH parameters. There has been a problem in properly obtaining the quadrature signal experimentally. The in-phase signal is usually larger than the quadrature signal and therefore a slight misadjustment of phase can cause the signal to be distorted. Alternative schemes have been suggested (2, 3) that generate phase invariant spectra. However, such methods mix the in-phase and quadrature components, and definable TDH parameters are changed or lost.

The original work of Hyde and Dalton (4) used the quadrature signals because these signals showed the nonlinear effects so well. The in-phase signals do show sensitivity to motion (in nearly the same way as the out of phase signals) but they have line shapes complicated by the existence of large, linear, motion-insensitive components contributing to the signal. Therefore, it is desirable to construct simple phase-independent spectra that predominantly retain the idea that the quadrature signal is the signal of choice.

Below, I outline a method of constructing ratio parameters that are independent of phase but that reduce exactly to the TDH parameters. The correlate to the above proposition is that with a definition of one additional field position, the TDH parameters can be made phase invariant.

Let us first define $I(H)$ and $Q(H)$ as the true in-phase and phase-quadrature signal intensities at field value H. $I'(H)$ and $Q'(H)$ are the components of the signals rotated by p:

$$I'(H) = \cos(p)I(H) + \sin(p)Q(H)$$
$$Q'(H) = \cos(p)Q(H) - \sin(p)I(H).$$

Now assume that the signals are known at three different field values, which we call H', H'' and Hr. From the above definitions of $I'(H)$ and $Q'(H)$, one can easily see that the quantity $[I'(H')\,I'(Hr) + Q'(H')\,Q'(Hr)]$ is phase invariant. Let us define a ratio parameter $R(H''/H', r)$, where the r refers to the reference field Hr. The ratio parameter is

$$R(H''/H', r) = \frac{I'(H'')\,I'(Hr) + Q'(H'')\,Q'(Hr)}{I'(H')\,I'(Hr) + Q'(H')\,Q'(Hr)}.$$

The above ratio parameter is independent of the phase of the modulation. Now we find a reference field (Hr) such that $I'(Hr) = 0$. This position is called Hr^*. Using Hr^* the ratio parameter reduces to

$$R(H''/H', r^*) = \frac{Q'(H'')}{Q'(H')}.$$

If the phase has been set such that the quadrature signal is the true quadrature signal, then the above ratio parameter is the TDH parameter. The above result may be stated another way: the definition of Hr^* makes the TDH parameters phase independent.

For the above definitions to be useful the true in-phase second harmonic absorption signal must vanish when the quadrature signal is not zero. Examination of the in-phase second harmonic absorption signal shows a position in from the turning points where these signals cross the axis and so

are zero. This has been observed both experimentally (3) and theoretically (5) for all motional times of interest. If a field value were used (by convention, for example, as a specified number of Gauss from H') where $I(Hr^*) = 0$ then the ratio signals so measured would reduce to the TDH parameters. Such ratio parameters would be phase invariant and independent of the interference from in-phase components.

No initial adjustment of phase setting is necessary, as is currently the case with the phase null method (1, 6). Two signals that are 90° apart can be easily obtained with the conventional spectrometer, or by the method outlined by Watanabe (7). Appropriate phasing such that $I'(Hr^*) = 0$ would require minimal computer manipulations. The full processing of ratio parameters could be done by computer.

REFERENCES

1. Thomas, D. D., L. R. Dalton, and J. S. Hyde. 1976. Rotational diffusion studied by passage saturation transfer electron paramagnetic resonance. *J. Chem. Phys.* 65:3006–24.
2. Vistnis, A. I. 1982. Magnetic hysteresis STEPR spectroscopy. *In* Abstracts of 24th Annual Rocky Mountain Conference. 87.
3. Hemminga, M. A., P. A. DeJager. 1981. Magnitude STEPR spectroscopy. *J. Magn. Res.* 43:324–7.
4. Hyde, J. S., and L. R. Dalton. 1972. Very slowly tumbling spin labels: adiabatic rapid passage. *Chem. Phys. Lett.* 16:568–75.
5. Perkins, R. C., T. Lionel, B. H. Robinson, L. A. Dalton, and L. R. Dalton, 1976. Saturation transfer spectroscopy: signals sensitive to very slow molecular reorientation. *Chem. Phys.* 16:393–404.
6. Hyde, J. S., and D. D. Thomas. 1980. Saturation transfer spectroscopy. *Annu. Rev. Phys. Chem.* 31:293–317.
7. Watanabe, T., T. Sasaki, K. Sawatari, and S. Fujiwara. 1980. A new detection system of STEPR spectroscopy by a Fourier transform technique. *J. Appl. Spectrosc.* 34:456–60.