

ON NMR PROBING OF THE KINETICS OF A FREE-ELECTRON LASER-INDUCED CHEMICAL EXCHANGE

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Abstract

Determination of the rate constants of chemical exchange reactions (at dark conditions, Figure 1) and the quantum yields of photo-induced chemical exchange

(PICE, in particular, molecular photoisomerization reactions) is an efficient application of NMR spectroscopy [1,2].

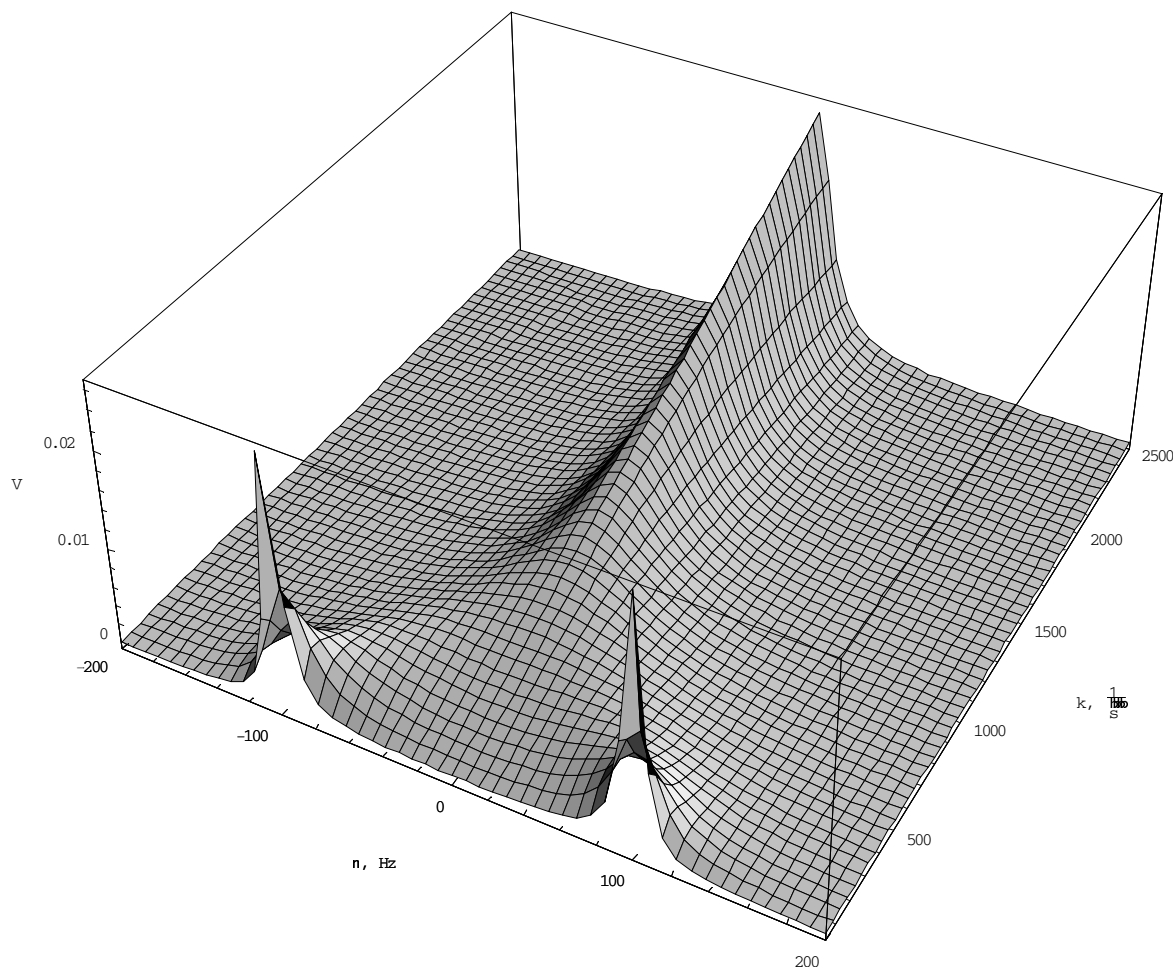
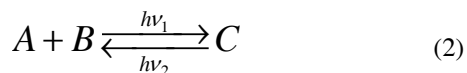


Figure1: Calculated NMR line-shape for a two-site chemical exchange at dark condition ($T_1=T_2=10$ c, $\Delta\nu=200$ Гц, the rate constant (k) changes from 38 to 2500 c^{-1}).

We are proposed a combined approach for study the kinetics of photo-induced chemical exchange (PICE)

reactions (see (1), (2)), which involves a free-electron laser (FEL) and NMR spectroscopy [3].



Continuous and pulse irradiation of the chemical system in the presence of PICE can be achieved using FEL.

THEORETICAL

Based on the analytical equations derived in the work we consider the time-dependent dynamics of variation of the instant NMR line shape for two-site chemical exchange.

$$v(t) = \text{Im} \left[e^{(R_0 + i\Delta\nu)t} \bar{G}_0 - i\omega \int_0^t e^{-(R_0 + i\Delta\nu)(t-\tau)} \left(e^{-R_0\tau} \bar{M}_{k0} - M_0 R_1^{-1} (e^{-R_0\tau} - I) \Gamma \cdot \bar{P} \right) d\tau \right] \quad (3)$$

If one induce an abrupt increase in the rate constant of chemical exchange (for example, by quickly heating the system or PICE), then the NMR line shape will change with time, ultimately reaching another new steady state. Our calculations show that there are beats and

oscillations (on the NMR line shape) damped with time (see Figure 2, (3)).

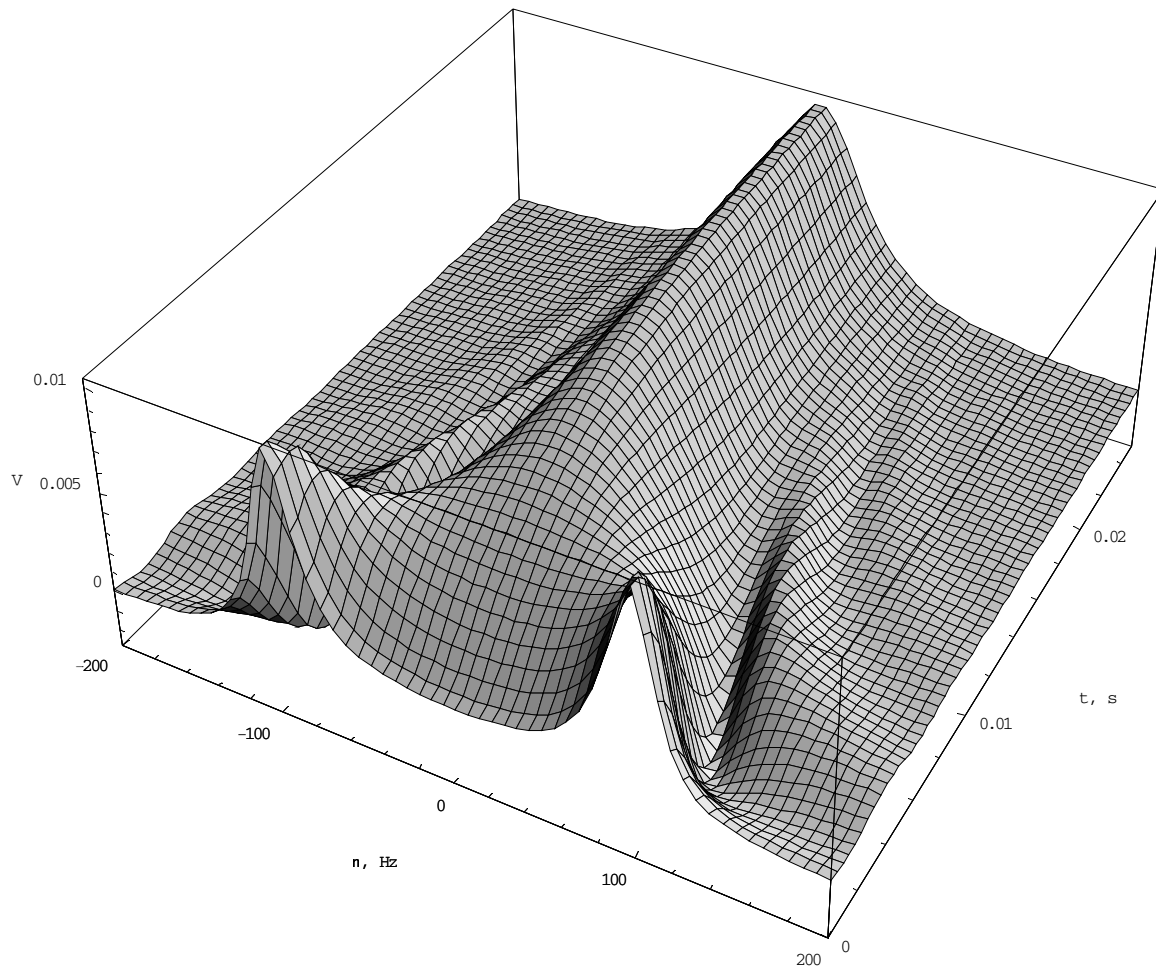


Figure 2: Calculated time-dependent NMR line-shape for a two-site chemical exchange at photo-induced chemical exchange condition ($T_1=T_2=10$ c, $\Delta\nu=200$ Гц, k changes from 100 to 2500 c^{-1} (at abrupt increase)).

CONCLUSION

The information about the time-dependent instant line shapes provides possibility to predict the real kinetics of PICE. Prospective objects are molecular conformers and spin isomers. So, FEL can be used in the setup for PICE studies in combination with a NMR spectrometer.

REFERENCES

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