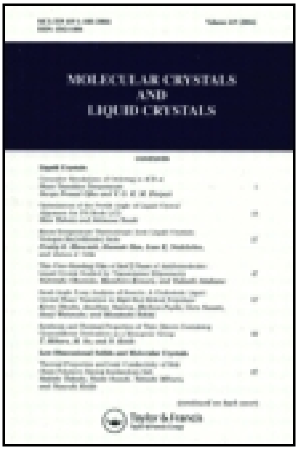

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Vibrational Relaxation of Guest Molecule in Host Crystal

V. Yakhot [a]

[a] Department of Structural Chemistry, Chemical Physics, The Weizmann Institute of Science, Rehovot, Israel

To cite this article: V. Yakhot (1976): Vibrational Relaxation of Guest Molecule in Host Crystal, Molecular Crystals and Liquid Crystals, 32:1, 91-95

To link to this article: http://dx.doi.org/10.1080/15421407608083630

Mol. Cryst. Liq. Cryst., 1976, Vol. 32, pp. 91–95
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Printed in Holland

Vibrational Relaxation of Guest Molecule in Host Crystal

V. YAKHOT

Department of Structural Chemistry and Chemical Physics, The Weizmann Institute of Science, Rehovot, Israel

The quantitative theory of multiphoton vibrational relaxation of a molecule in a host crystalline matrix is developed. A simple closed formula for the relaxation rate is obtained. Interpretations of several experimental results based on this formula are discussed.

I INTRODUCTION

The current interest in the problem of multiphonon vibrational relaxation of a guest molecule in the matrix of a crystalline host has been stimulated by the excellent experimental work of Dubost, Abouaf–Marquin and Legay.[1] The most recent theories to appear[2,3] have explained the new effects reported by the above authors, thus emphasizing the importance of the multi-phonon nature of the relaxation process. These very interesting theories of harmonic oscillator relaxation in the host crystal include free parameters, and are therefore of semi-quantitative character. We would like to present here an attempt to develop the quantitative theory of vibrational relaxation of a guest molecule in a crystal.

II THEORY

Let us consider a molecule in the host crystal. Let V be the potential of molecule-matrix interaction. It is assumed that the main contribution to V comes from interaction with the nearest molecule-crystal atoms. For simplicity we take the interactions between molecular atoms and crystal atoms to be the same for all atoms of the molecule; this is not an essential assumption and a generalization can readily be made.

Using these assumptions and the model geometry of Ref. 4 one can write:

$$V = \eta V\left(y_0 - \frac{x}{2} + y\right) \simeq \eta V_0(y) - \frac{\eta}{2} x \frac{\partial V(y_0 + y)}{\partial x} \tag{1}$$

where $V_0(y)$ is the term which does not depend on x, y_0 is the equilibrium molecule atom-to-nearest matrix atom distance, η is the number of nearest neighbours, and, x, y are the vibrational displacements of molecular and matrix atoms, respectively. In obtaining Eq. (1) we took into account the fact, which is very important for our theory, that in the case of multiphonon relaxation (units of $\hbar$ are used throughout)

$$\left|\frac{E_n - E_{n-1}}{\omega_D}\right| \gg 1, \tag{2}$$

and in fact this inequality may be considered as the definition of the multiphonon process. In Eq. (2) E_n and ω_D are, respectively, the vibrational-energy levels of the molecule and the Debye frequency of the crystal.

Using a well-known procedure[4,5] one can write the expression for the probability of the $n \rightarrow n - 1$ transition of the oscillator:

$$\mathscr{P}_{n,n-1} = \frac{\eta^2}{4} |x_{n,n-1}|^2 \int_{-\infty}^{\infty} dt\, e^{it(E_n - E_{n-1})} G(t) \tag{3}$$

$$G(t) \simeq \left\langle N \left| \frac{\partial V[y_0 + y(t)]}{\partial x} \frac{\partial V[y_0 + y(0)]}{\partial x} \right| N \right\rangle \equiv \langle N | F(t) F(0) | N \rangle \tag{4}$$

where F is the molecule-crystal force. It is possible to show that if one can represent molecule-crystal force:

$$\frac{\partial V(y_0 + y)}{\partial x} = a_0\left(1 + \sum_{n>0} \alpha_n y^n\right) \tag{5}$$

one can get without strong assumptions:

$$\mathscr{P}_{n,n-1} \equiv \frac{1}{\tau_{n,n-1}} = a_0^2 \frac{v^2}{4} |x_{n,n-1}|^2 \sqrt{\frac{\pi}{F}}\, e^c \exp\left[-\frac{(E_n - E_{n-1})^2}{4F}\right] \tag{6}$$

where

$$\begin{aligned} c &= (2\alpha_2 + \alpha_1)^2 \sum_{\mathbf{q}} \frac{1}{2M\omega_{\mathbf{q}}} (2n_{\mathbf{q}} + 1) \\ F &= \frac{\alpha_1^2}{2M} \sum_{\mathbf{q}} (n_{\mathbf{q}} + \tfrac{1}{2}) \omega_{\mathbf{q}}. \end{aligned} \tag{7}$$

These formulae are exact if the molecule-crystal interaction is exponential.

III DISCUSSION

We have obtained a simple, closed expression (Eq. 6) for the rate of multiphonon vibrational relaxation of a molecule in a host matrix. We consider three important consequences of this result.

a) If

$$\frac{(E_n - E_{n-1})^2}{4F} \gg 1 \tag{8}$$

even very small variations of n_q can cause very large changes in the vibrational lifetime. Previous theories[2,3] led to the same qualitative conclusion and explained the very intriguing temperature-dependence of this lifetime found experimentally:[1] the increase of rate of relaxation of the CO molecule in solid Ar with increasing temperature starts at a temperature which is much lower than the Debye temperature. The cause of this effect is not obvious since at such a temperature the phonon energy is small compared with the zero-point energy of the solid, so at a first sight effects involving the phonons should be negligibly small.

b) Even a small deviation from harmonicity can have important new consequences: if $E_n - E_{n-1} > E_{\hat{n}} - E_{\hat{n}-1}$ and Eq. (8) is fulfilled, it may occur that

$$\tau_{n,n-1} \gg \tau_{\hat{n},\hat{n}-1}$$

This would be very important in cases in which vibrational and radiative relaxation processes compete with one another. It is possible that

$$\tau_{n,n-1} \ll \tau_R \ll \tau_{n-1,n-2} \tag{9}$$

where τ_R is the radiative lifetime.

We calculated the transition probabilities $\mathscr{P}_{n,n-1}$ of Ne_2^* relaxation in solid Ne matrix. The results are given in Table 1. The radiative lifetime of Ne_2^* $\tau_R \simeq 5 \cdot 10^{-6}$ sec (Eq. 6) and one can conclude that almost all molecules

TABLE I

Transition $n \rightarrow n-1$	$1 \rightarrow 0$	$2 \rightarrow 1$	$3 \rightarrow 2$	$4 \rightarrow 3$	$5 \rightarrow 4$
Energy spacing $\Delta E_{n,n-1}$ (cm^{-1})	537	496	454	412	370
Lifetime $\tau_{n,n-1}$ (sec)	10	$1 \cdot 10^{-2}$	$4 \cdot 10^{-5}$	$4 \cdot 10^{-}$	$8 \ 10^{-9}$

radiate from level $n = 3$. In fact, as follows from Table I, the relaxation *to* state $n = 3$ is very fast while the relaxation *from* this state is slow in comparison with radiative lifetime. The calculated lineshape is seen (Figure 1) to be in very good agreement with experiment (7) if the experimental resolution and random scatter is taken into account.

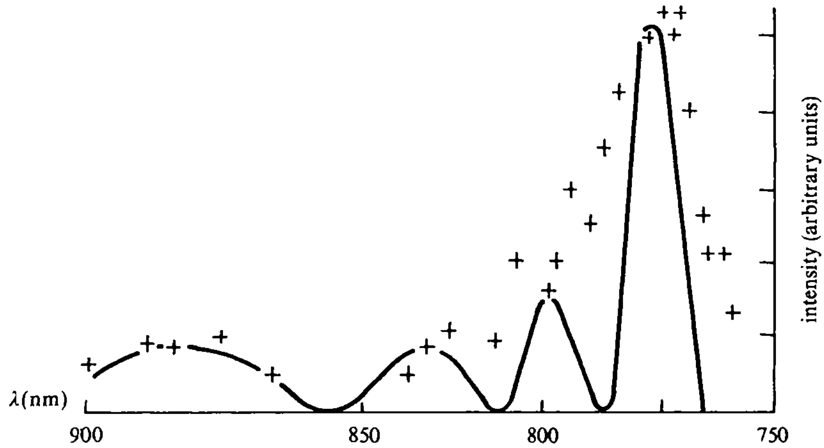

FIGURE 1 Emission spectra of Ne_2^* from solid Ne
+ experiment (2)
—— theory (present work)

Using Eq. (6) we calculated the vibrational relaxation rates of the excimers in solid, Ar, Kr and Xe. In all cases the relaxation is very fast compared with the radiative lifetime ($\tau_R \simeq 10^{-6}$ sec). It was calculated that $\tau_{1,0}(\mathrm{Ar}) \simeq 10^{-8}$ sec, $\tau_{1,0}(\mathrm{Kr}) \simeq 10^{-11}$ sec, and $\tau_{1,0}(\mathrm{Xe}) \simeq 10^{-13}$ sec. This explains the ordinary free-excimer-like Gaussian lineshapes of the emission in these cases. One understands the relatively fast relaxation of these excimers if one recalls that the energy spacings $E_n - E_{n-1}$ of Ar_2^*, Kr_2^* and Xe_2^* are smaller than the corresponding spacings for Ne_2^*.

c) The rate of vibration relaxation depends very strongly on the phonon spectrum of the solid, and especially on the structure of the high-energy tail of this spectrum. It follows from Eqs. (6) and (7) that if the contribution of high frequencies to Eq. (7) is appreciable the relaxation is more rapid. Moreover, the local modes associated with impurities or with the relaxing molecule itself can be very important because they also make F of Eq. (7) larger, and thus increase the rate given by Eq. (6).

A solid–solid phase transition can be accompanied by changes in the phonon spectrum and thus the relaxation properties of a guest molecule can be different below and above critical point. Further, the molecule-crystal coupling constant α_1 can increase or decrease in this process, and this too can affect the vibrational lifetime. So below and above the transition temperature of a matrix the relaxation properties of a guest molecule may be quite different. This is illustrated qualitatively very well by the unusual emission of Xe_2^* in solid Xe.[8].

The authors of Ref. 8 explained the change in the spectrum of Xe_2^* in Xe crystal they observed at 56°K in terms of a phase transition at this temperature. This conclusion is in accord with our theory if one assumes that the relaxation below this temperature is very efficient, but is slow just above the transition temperature. The free-excimer-like spectrum at very low temperatures then originates from the "low-temperatures phase", while both the two-peak spectrum and the high-temperature free-excimer-like spectrum originate from the "high-temperature phase".

References

1. H. Dubost, L. Abouaf-Marquin, and F. Legay, *Phys. Rev. Lett.*, **29**, 145 (1972).
2. D. J. Diester, *J. Chem. Phys.*, **60**, 2692 (1974).
3. A. Nitzan, S. Mukamel, and J. Jortner, *J. Chem. Phys.*, **60**, 3929 (1974).
4. V. Yakhot, M. Berkowitz, and R. B. Gerber, *Chem. Phys.*, **10**, 61 (1975).
5. See for example, review S. H. Lin and H. Eyring, *Ann. Rev. Phys. Chem.*, **25**, 39 (1974).
6. P. K. Leichner, *Phys. Rev.*, **A8**, 815 (1973).
7. R. E. Packard, F. Reif, and Surko, *Phys. Rev. Lett.*, **25**, 1435 (1970).
8. O. Chechnovsky, A. Gedanken, B. Raz, and J. Jortner, *Sol. State Comm.*, **13**, 639 (1973).