

## Excimer formation as the relaxation of a nonlinear oscillator: Theory of $Y$ states

D. H. Dunlap and V. M. Kenkre

*Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131*

(Received 19 June 1987)

The existence of  $Y$  states in excimer-forming molecular crystals is addressed through a simple extension of an earlier model of the formation of excimers as occurring through the relaxation of a nonlinear oscillator. These  $Y$  states, which do not appear in solution, and have been observed in only some crystals, are intermediate states with partial excimeric character. Such states are shown to arise naturally in our model as a simple consequence of additional interactions that exist in the crystal, but not in solution, and to be associated with an abrupt (rather than gradual) transition as the strength of those interactions is varied.

### I. INTRODUCTION

Excimers in molecular crystals have come under active investigation in recent times, particularly from experimentalists.<sup>1-15</sup> Of the outstanding problems that these investigations present to the theorist, one is associated with the nature of the so-called  $Y$  states observed in some excimer-forming crystals. They are postulated<sup>7-13</sup> in order to account for observed portions of spectra which are neither as structured as monomeric spectra nor as broad and Stokes-shifted as true excimer spectra. These and other features such as the temperature dependence of the spectra<sup>12</sup> and the magnitude of the lifetime have led to the picture that  $Y$  states are intermediate states with partial excimeric character. Some of the recent experiments<sup>7-13</sup> have addressed specifically the existence of barriers in excimer potentials that would correspond to such intermediate states and to the measurement of the barrier parameters. The question of whether the  $Y$  states are intermediate states in the process of the time evolution (formation) of excimers has also been addressed carefully.<sup>13</sup> Despite this renewed experimental interest, the exact nature of the  $Y$  states is by no means understood. We address this problem in the present paper.

The basis of our present investigation is a model for excimer formation which we analyzed in an earlier publication<sup>16</sup> (which we will refer to henceforth as I). The feature we append to that model for our present purpose is the existence of additional interactions which would be absent in solution but present in crystals. Additional interactions which may hinder complete relaxation and therefore the formation of normal excimer states have already been suggested<sup>7-13,15</sup> as a possible source of  $Y$  states. The analysis in the present paper has been undertaken with two purposes in mind: One is the quantification, in the context of a simple and tractable model, of the qualitative suggestions in the literature concerning  $Y$  states. The other is the careful examination of the physics behind those suggestions. Such a careful examination is important because additional interactions which hinder relaxation need not necessarily lead to the formation of new intermediate *partially relaxed* states (they could simply lead to a change in the location of the

excimer states in the frequency spectrum).

We refer the reader elsewhere<sup>1-3</sup> for details concerning excimers and excimer-forming crystals but provide here a reminder of what constitutes the signature of an excimer and how the basic model we employ arises from observed spectra. Lack of mirror symmetry between absorption and emission spectra, the latter being considerably broad and rather structureless, constitutes, along with a characteristically long lifetime, the primary identifying observational feature of excimers.<sup>1,2</sup> In solutions, where they were first observed, their formation is understood as occurring through the initial electronic excitation of a molecule followed by its migration in the solution until it meets an unexcited molecule with which it forms a complex.<sup>1,2</sup> While the initial excitation thus corresponds to the structured absorption characteristic of the single molecule (monomer), the emission has the quite different features peculiar to the complex. A similar picture<sup>16,17</sup> may be developed for excimers in crystals by replacing the migration process (which can occur in solution but not in crystals) by a relaxation process along a relatively flat potential. The spectral features thus dictate that the excimer potential in the electronically excited state be highly nonlinear. The model analyzed in I, therefore, looks upon the formation of an excimer as simply the relaxation of a crystal (for simplicity a chain of masses interacting via nearest-neighbor harmonic springs) in which one of the springs (the one connecting the excimer-forming pair of molecules) is made suddenly nonlinear and placed out of equilibrium by the process of absorption of light. On the basis of several given nonlinearities of the potential, our earlier analysis showed<sup>16</sup> explicitly how the formation of the excimer occurs in time and how the nonlinear nature of the excimer interaction manifests itself in observables such as the time-dependent spectrum.

An example of a crystal in which  $Y$  states occur is  $\alpha$ -perylene. It has been observed that the  $Y$ -state emission and the fully relaxed excimer (" $E$ -state") emission are separated by an energy barrier of about  $300\text{ cm}^{-1}$ , and it has been suggested that in  $\alpha$ -perylene, the full relaxation to the  $E$  state is prevented by the constraints that the rest of the lattice puts on the excimer pair.<sup>15</sup> Recent time-

resolved experiments<sup>13</sup> have clearly shown that in  $\alpha$ -perylene, the  $Y$  state is indeed a precursor state in the formation of the  $E$  state. This conclusion, which is in contradiction to an earlier one,<sup>12</sup> is based on the observation that the rise time of the  $E$  state coincides with the decay time of the  $Y$  state at all temperatures for which both states are observable. Time-resolved measurements on *pyrene* have shown that  $\alpha$ -perylene may not be the only excimer-forming crystal to exhibit a precursor state. Evidence of a precursor in *pyrene* has been found and that state has been dubbed the “ $B$  state.”<sup>14</sup>

The present paper is set out as follows. In Sec. II we extend the model studied in I to higher dimensions and analyze the time dependence of excimer relaxation. In Sec. III we show that the presence of additional interactions in higher dimensions results in the formation of a partially relaxed state (the  $\gamma$  state). We also examine the conditions under which the state occurs, show that the formation of the state is associated with an *abrupt* transition, obtain effective potentials for excimer relaxation which clarify the process of the formation of the  $Y$  state, and investigate the dependence of the height of the barrier separating the  $Y$  state from the  $E$  state on the lattice interaction. A discussion and concluding remarks constitute Sec. IV.

## II. TIME DEPENDENCE OF NONLINEAR RELAXATION IN TWO AND THREE DIMENSIONS

As in I we investigate the formation of an excimer in a crystal by analyzing the vibrations of a lattice of masses (molecules) interacting via nearest-neighbor springs (harmonic interaction potentials), one of the springs (the “excimer spring”) being made suddenly *nonlinear* and placed out of equilibrium by the absorbed light. The process of interest is the relaxation of this excimer spring to equilibrium. The specific quantity we focus on is the separation of the excimer-forming pair of molecules connected by the nonlinear spring as a function of time. Whereas the lattice studied in I was one dimensional for simplicity,

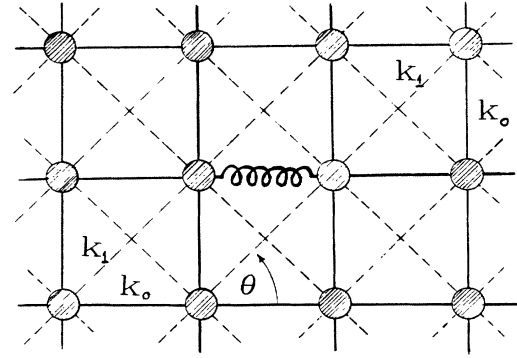


FIG. 1. The two-dimensional square lattice with “horizontal” and “vertical” harmonic springs with spring constant  $k_0$  (see text), “diagonal” springs with spring constant  $k_1$  making an angle  $\theta$  with the horizontal axis, and the nonlinear excimer interaction, represented by the explicitly drawn spring, which is turned on by the process of light absorption.

here we are particularly interested in additional effects of the extension of that model to higher dimensions. We begin with a two-dimensional lattice pictured in Fig. 1. We generalize the one-dimensional evolution equation used in I, viz.,

$$\begin{aligned} M d^2 x_m / dt^2 = & -k_0(2x_m - x_{m-1} - x_{m+1}) \\ & + (\delta_{m,0} - \delta_{m,1}) \\ & \times [k_0(x_0 - x_1) - V'(x_1 - x_0)], \end{aligned} \quad (2.1)$$

where  $x_m$  is the deviation from equilibrium of the  $m$ th molecule of mass  $M$  in the chain (one-dimensional lattice),  $k_0$  is the spring constant of any spring in the lattice before the absorption of light, and  $V$  is the nonlinear potential of the excimer-forming pair located at sites 0 and 1, to the two-dimensional form

$$\begin{aligned} M d^2 x_{m,n} / dt^2 = & -2(k_0 + 2k_1 \cos^2 \theta)x_{m,n} + k_0(x_{m+1,n} + x_{m-1,n}) \\ & + k_1 \cos^2 \theta(x_{m+1,n+1} + x_{m-1,n-1} + x_{m+1,n-1} + x_{m-1,n+1}) \\ & + k_1 \sin \theta \cos \theta (y_{m+1,n+1} + y_{m-1,n-1} - y_{m+1,n-1} - y_{m-1,n+1}) \\ & + \delta_{n,0}(\delta_{m,0} \delta_{m,1}) [k_0(x_{0,0} - x_{1,0}) - V'(x_{1,0} - x_{0,0})], \end{aligned} \quad (2.2)$$

$$\begin{aligned} M d^2 y_{m,n} / dt^2 = & -2(k_0 + 2k_1 \sin^2 \theta)y_{m,n} + k_0(y_{m+1,n} + y_{m-1,n}) \\ & + k_1 \sin^2 \theta (y_{m+1,n+1} + y_{m-1,n-1} + y_{m+1,n-1} + y_{m-1,n+1}) \\ & + k_1 \sin \theta \cos \theta (x_{m+1,n+1} + x_{m-1,n-1} - x_{m+1,n-1} - x_{m-1,n+1}). \end{aligned} \quad (2.3)$$

In (2.2) and (2.3), the double index  $(m,n)$  identifies the mass as  $m$ th along the  $x$  axis and  $n$ th along the  $y$  axis,  $x$  and  $y$  are the respective components of the deviation of the mass from equilibrium, the excimer-forming pair is at

$(0,0)$  and  $(0,1)$ , and  $k_0$  is the (harmonic) spring constant of any of the horizontal or vertical springs in the lattice before the absorption process. By a *horizontal* spring we mean that which connects the mass at  $(m,n)$  to the ones

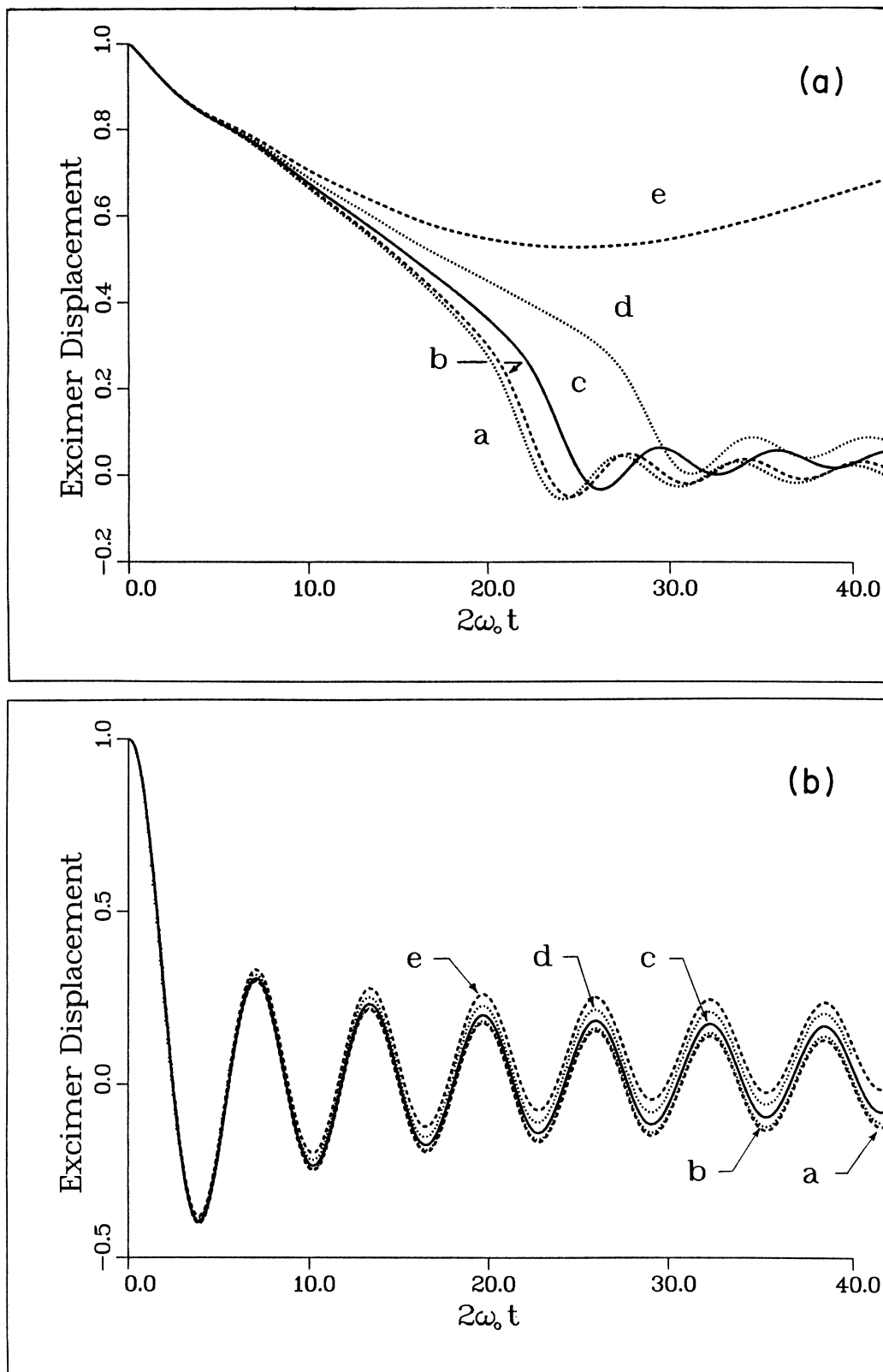


FIG. 2. The formation of the excimer: the time dependence of the relaxation of the excimer coordinate  $\zeta(t)$  shown for five different values of  $\omega_1/\omega_0$ : (a) 0, (b) 0.025, (c) 0.05, (d) 0.075, and (e) 0.1. Time  $t$  is plotted in units of  $(1/2\omega_0)$ . Units of the excimer coordinate  $\zeta$  are scaled such that 0 represents the value at the minimum of the excimer potential and 1 the initial value at excitation. The excimer potential is taken to be nonlinear and representative of excimer-forming crystals in (a) but linear in (b). The equilibrium position to which relaxation occurs changes continuously in (b) but appears to undergo a transition in (a) from curve  $d$  to curve  $e$ .

at  $(m \pm 1, n)$  and by a *vertical* spring we mean that which connects it to the ones at  $(m, n \pm 1)$ . The *diagonal* spring which connects the mass at  $(m, n)$  to the ones at  $(m \pm 1, n \pm 1)$  has the spring constant  $k_1$ . The angle the diagonal spring makes with the  $x$  axis is  $\theta$ . The "defect term" analogous to the last term in (2.1) appears in (2.2) but not in (2.3) because we assume here, for the sake of simplicity, that the single spring made nonlinear by the process of absorption lies in the  $x$  direction.

In order to avoid confusion, we depart from the notation in I and use here the symbols  $\zeta$  and  $\psi$ , rather than  $y$ , to describe the respective components ( $x$  and  $y$ ) of the differences between the deviations from equilibrium of masses which are neighbors in the  $x$  direction:

$$\zeta_{m,n} = x_{m+1,n} - x_{m,n}, \quad (2.4)$$

$$\psi_{m,n} = y_{m+1,n} - y_{m,n}. \quad (2.5)$$

The method described in I allows us to solve formally for the  $\zeta$ 's and  $\psi$ 's from (2.2) and (2.3). The result for the quantity of interest, viz.,  $\zeta_{0,0}(t)$ , is

$$\begin{aligned} \zeta_{0,0}(t) = & \eta_{0,0}(t) \\ & + (1/M) \int_0^t dt' \phi(t-t') \\ & \times [k_0 \zeta_{0,0}(t') - V'(\zeta_{0,0}(t'))]. \end{aligned} \quad (2.6)$$

This is a nonlinear integral equation which, as described in I, can be solved to arbitrary accuracy through numerical methods. The nonlinearity arises from the dependence of  $V'$  on  $\zeta_{0,0}$ , i.e., from the excimer-restoring force which is nonlinear in the excimer coordinate. The initial condition term  $\eta_{0,0}(t)$  vanishes for the excitation conditions which we have assumed.<sup>16</sup> On dropping the subscripts on  $\zeta$ , and defining  $\omega_0$  and  $v$  through  $\omega_0^2 = k_0/M$  and  $v = V/M$ , respectively, we can rewrite (2.6) as

$$\zeta(t) = \int_0^t dt' \phi(t-t') [\omega_0^2 \zeta(t') - v'(\zeta(t'))]. \quad (2.7)$$

Equation (2.7) is the starting point for the exploration of excimer relaxation in any number of dimensions. The kernel  $\phi(t)$  is a "propagator" which describes relaxation or wave propagation in a lattice without the "defect" of the excimer nonlinearity and equals  $(2/\omega_0)J_1(2\omega_0 t)$  in a one-dimensional infinite lattice.<sup>16</sup> Exact expressions for the two-dimensional lattice of Fig. 1 as well as for the corresponding three-dimensional lattice are given in the Appendix. In order to simplify the labor involved in obtaining explicit solutions of (2.7) in the time domain, we assume that  $\theta$  is small enough for the coupling along the diagonal to nearest neighbors to be entirely through the vibrations in the  $x$  direction and take the ratio of the diagonal spring constant to the horizontal (or vertical) one to be small ( $k_1/k_0 \ll 1$ ). Equation (A2) then reduces to

$$\tilde{\phi}(\epsilon) \cong (1/\omega_0^2) [1 - (\epsilon^2 + 4\omega_1^2)^{1/2} / (\epsilon^2 + 4\omega_0^2)^{1/2}], \quad (2.8)$$

where  $\omega_1^2 = k_1/M$  and  $\omega_0^2 = k_0/M$ . We note in passing that on putting  $\omega_1 = 0$ , (2.8) yields the one-dimensional result, i.e., the Laplace transform of  $(2/\omega_0)J_1(2\omega_0 t)$ , as indeed it should. The effect of the diagonal springs may

be seen explicitly in (2.8).

The substitution of the inverse Laplace transform of (2.8) in (2.7) allows one to solve for the time dependence of the excimer-pair coordinate. We carry out the solution numerically and plot the results in Fig. 2(a). Several candidates for an analytic representation of the nonlinear potential  $V$  exist in the literature. In I we have analyzed three<sup>18</sup> of them explicitly: the Morse potential, the Rydberg potential, and the Beckel-Findley potential. It is straightforward to include those of any other explicit forms of the potential in our solution of (2.7). However, the fact that a considerable part of the solution procedure is numerical makes it much preferable to take an empirically given (or sketched) form for the potential. The form we have chosen here incorporates all the physical characteristics required by spectral observations (see Sec. I) and can be viewed explicitly as curve (a) of Fig. 5.

Figure 2(a) shows the separation of the excimer pair as a function of time for several relative strengths of the diagonal spring, specifically for several values of the ratio  $\omega_1/\omega_0$ . When  $\omega_1/\omega_0$  is zero, i.e., when the system is one-dimensional, the excimer pair relaxes to the minimum of the interaction potential  $V$ . When  $\omega_1/\omega_0$  is not zero, the excimer-pair separation at equilibrium is larger. The reason for this behavior is obvious. When diagonal interactions are included, the molecules to the right and to the left of the excimer pair are connected via an infinite number of indirect paths, as well as directly through the excimer pair. The indirect interactions tend to oppose the lattice distortion which accompanies the contraction of the excimer pair, and their effect increases with the strength of the diagonal spring. This hindering effect of the lattice is not surprising and would be obtained even if the potential of the electronically excited molecular pair were harmonic with a mere shift in its equilibrium position. This linear case, which provides the standard model<sup>19,20</sup> for absorption and emission in crystals with mirror-symmetric spectra (i.e., those in which excimers are not observed), is represented in Fig. 2(b). Comparison of Figs. 2(a) and 2(b) shows that the hindering effect of the lattice is present in both cases. However, a careful inspection of Fig. 2(a) reveals a surprising feature not present in Fig. 2(b): The separation at which the excimer pair comes to equilibrium appears to undergo a *sudden transition* as the value of  $\omega_1/\omega_0$  is varied (note the different appearance of curve *e*). As we shall see below, this transition is intimately connected with the *Y* state. A detailed examination of the transition, in particular of its discontinuous nature, is carried out in the following section through time-independent arguments.

### III. ABRUPT TRANSITION AND THE EMERGENCE OF THE Y STATE

In order to examine the transition suggested by Fig. 2(a), we plot the dependence of the excimer equilibrium separation on  $\omega_1/\omega_0$  in Fig. 3. The transition is found to be indeed abrupt. On the left of the transition, i.e., when  $\omega_1/\omega_0$  is smaller than the transition value, the hindering effect of the lattice results merely in a (relatively) slight increase in the equilibrium separation. However, at the

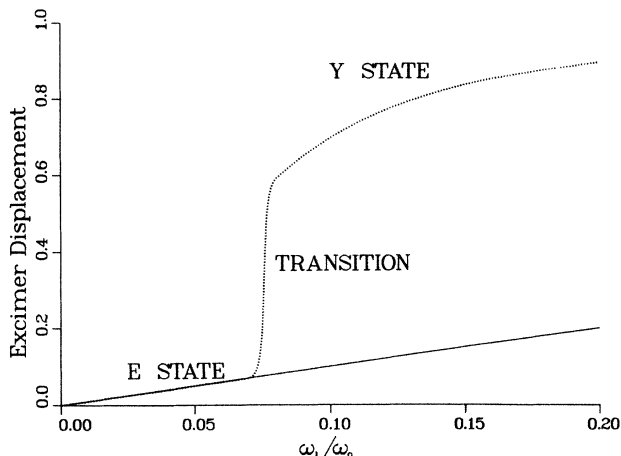


FIG. 3. The equilibrium position  $\zeta(\infty)$  of the excimer corresponding to Fig. 2(a) plotted as a function of  $\omega_1/\omega_0$ . The transition occurs at  $\omega_1/\omega_0=0.075$  and is clearly seen to be abrupt. The  $E$  state and the  $Y$  state are indicated. The dotted line represents the system under investigation. The solid line corresponds to a system in which the excimer potential is linear [as in the case of Fig. 2(b)].

transition value of  $\omega_1/\omega_0$ , the increase is discontinuous. The significance of the discontinuity is that, at and beyond the transition value of  $\omega_1/\omega_0$ , the hindering effect of the lattice has the nontrivial consequence that the excimer acquires an *additional* equilibrium separation. To understand the source of this interesting phenomenon, we return to (2.7) and take Laplace transforms to obtain

$$\bar{\kappa}(\epsilon)\bar{\zeta}(\epsilon) = -\int_0^\infty dt e^{-\epsilon t} v'(\zeta(t)), \quad (3.1)$$

$$\bar{\kappa}(\epsilon) = [1/\bar{\phi}(\epsilon)] - \omega_0^2. \quad (3.2)$$

Although numerical work was necessary in the last section to invert (3.1) and obtain  $\zeta(t)$  for all  $t$ , analytic means can be employed to draw from it exact conclusions concerning  $\zeta(\infty)$ , the equilibrium value of the excimer coordinate. On multiplying (3.1) by  $\epsilon$ , taking the limit  $\epsilon \rightarrow 0$  and invoking an Abelian theorem concerning asymptotic values, we get

$$\bar{\kappa}(0)\zeta(\infty) = \{[1/\bar{\phi}(0)] - \omega_0^2\}\zeta(\infty) = -v'(\zeta(\infty)). \quad (3.3)$$

We note here that although the Laplace transform of  $v'(\zeta(t))$  is by no means  $v'(\bar{\zeta}(\epsilon))$ , the limit of  $\epsilon\{\int_0^\infty dt e^{-\epsilon t} v'(\zeta(t))\}$  as  $\epsilon \rightarrow 0$  is indeed equal to  $v'(\zeta_0^\infty)$ .

Equation (3.3) has a remarkably simple form and can be solved at once to obtain the equilibrium value of the excimer coordinate once the time integral of the propagator, viz.  $\bar{\phi}(0)$ , and the nonlinear "force"  $v'$  are known. It also provides us immediate insight into the formation of the  $Y$  state: The state arises only when (3.3) has more than one solution for  $\zeta(\infty)$ . The physical meaning of (3.3) is quite transparent. At equilibrium, the excimer pair is acted upon by two forces: the nonlinear excimer pair force which tends to pull the pair together and is represented by the right-hand side of (3.3), and an

effective restoring force exerted by the lattice which tends to oppose the contraction of the excimer pair. The latter is represented by the left-hand side of (3.3) and corresponds to an effective spring constant  $[1/\bar{\phi}(0)] - \omega_0^2$ . When, as in the one-dimensional chain, hindering interactions arising from the (diagonal)  $k_1$  springs are absent,  $\bar{\phi}(0)$  equals  $1/\omega_0^2$ , and the effective spring constant  $\bar{\kappa}(0)$  vanishes. The equilibrium state of the excimer pair is then at the minimum of the nonlinear potential  $v$ , and there is only a single excimer state, the  $E$  state. This situation also occurs for excimers in solution for which the interactions with the rest of the "lattice" are negligible. When, however, those interactions are present, two effects can occur. One is a simple shift of the  $E$ -state equilibrium coordinate caused by the addition of the left-hand side term in (3.3). The other, which only occurs when the effective spring constant  $\bar{\kappa}(0)$  exceeds a critical value, is that multiple minima appear in the total potential  $v(\zeta) + \frac{1}{2}\bar{\kappa}(0)\zeta^2$ . The additional minimum in the effective potential represents the  $Y$  state.

Following a standard method employed in the mean field theory of phase transitions,<sup>21</sup> we plot the right- and left-hand sides of (3.3) separately in Fig. 4. The intersection yields the equilibrium separation  $\zeta(\infty)$ . The characteristics of the nonlinear potential  $v(\zeta)$  dictated by observed excimer spectra (see Sec. I) are reflected in the features of the force  $v'(\zeta)$  shown in Fig. 4. The value of  $\zeta$  at which the  $v'$  curve crosses the  $\zeta$  axes is the equilibrium separation of the excimer pair in the absence of the  $k_1$  interactions. Around that region, the force has a linear re-

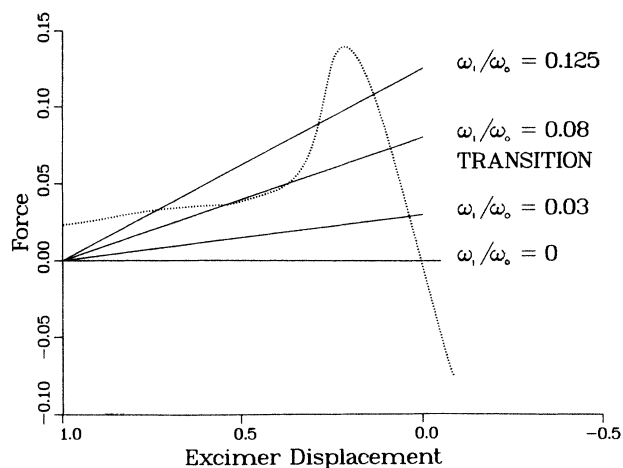


FIG. 4. The analysis of the transition based on an exact treatment of (2.7) in the infinite  $t$  limit, through a graphical solution of (3.3). The dotted curve represents the nonlinear excimer force and the four solid lines represent the effective restoring force of the lattice for four respective values of  $\omega_1/\omega_0$ : (a) 0, (b) 0.03, (c) 0.08, and (d) 0.125. The intersection of the solid lines with the dotted curve gives  $\zeta(\infty)$ , the equilibrium value of the excimer coordinate. Only an  $E$  state occurs for (a) and (b). Multiple solutions for (c) and (d) show that a  $Y$  state is also formed. Units of the excimer coordinate are as in Fig. 3, and those of the force are arbitrary.

storing nature. The  $\zeta$  origin is at the equilibrium separation of the unexcited  $k_0$  spring, where the excimer pair finds itself on electronic excitation. The restoring force of the lattice, represented by  $\bar{\kappa}(0)\zeta$ , is shown for four different values of  $\omega_1/\omega_0$ , i.e., of  $\bar{\kappa}(0)$ . The corresponding curves are simply straight lines of four different slopes. When the slope is zero, the intersection of the two curves is at the minimum of  $v(\zeta)$ . When it is larger than zero, one obtains either a single point of intersection, as in curves (a) and (b), or three points of intersection, as in curves (c) and (d). Curve (c) has been labelled by the word "transition" in Fig. 4 because it is in the neighborhood of (although beyond) the transition. A single point of intersection corresponds to a mere shift of the location of the  $E$  state. Multiple intersections signal the formation of the  $Y$  state. Of the three points of intersection, the middle one corresponds to a *maximum* of the total effective potential, whereas the other two represent true equilibrium states: The  $E$  state and the  $Y$  state.

In Fig. 5 we show the effective potential  $v(\zeta) + \frac{1}{2}\bar{\kappa}(0)\zeta^2$  for the five respective values of  $\omega_1/\omega_0$  shown in Fig. 2. Curve (a) corresponds to  $\omega_1/\omega_0=0$ , and therefore to  $\bar{\kappa}(0)=0$ , and thus describes the excimer potential we have

assumed for the calculations in this paper. As  $\omega_1/\omega_0$  becomes nonzero, the minimum of the effective potential shifts slightly through curves (b), (c), and (e). The single-excimer state, the  $E$  state, merely moves on the  $\zeta$  axis. Curve (e) corresponds to values of  $\omega_1/\omega_0$  larger than the critical value. The transition has occurred, and the additional minimum of the effective potential is visible: The  $Y$  state has now appeared. The inset in Fig. 5 is an enlargement of curve (e) made to exhibit the two minima clearly. Both Figs. 4 and 5 show unambiguously that when the  $Y$  state occurs, it does so at a location on the  $\zeta$  axis removed by a *finite* amount from the location of the  $E$  state.

Finally, we investigate the height of the barrier which separates the  $Y$  state from the  $E$  state. This quantity determines the observed temperature dependence of the relative strengths of the  $Y$  and  $E$ -state emission and has been examined in several recent experiments.<sup>7-13</sup> The dependence of the barrier height on  $\omega_1/\omega_0$ , as calculated in the context of our model, is shown in Fig. 6. There is no barrier for values of  $\omega_1/\omega_0$  less than the threshold value since there is then no  $Y$  state. For higher values of  $\omega_1/\omega_0$ , the barrier height increases as shown.

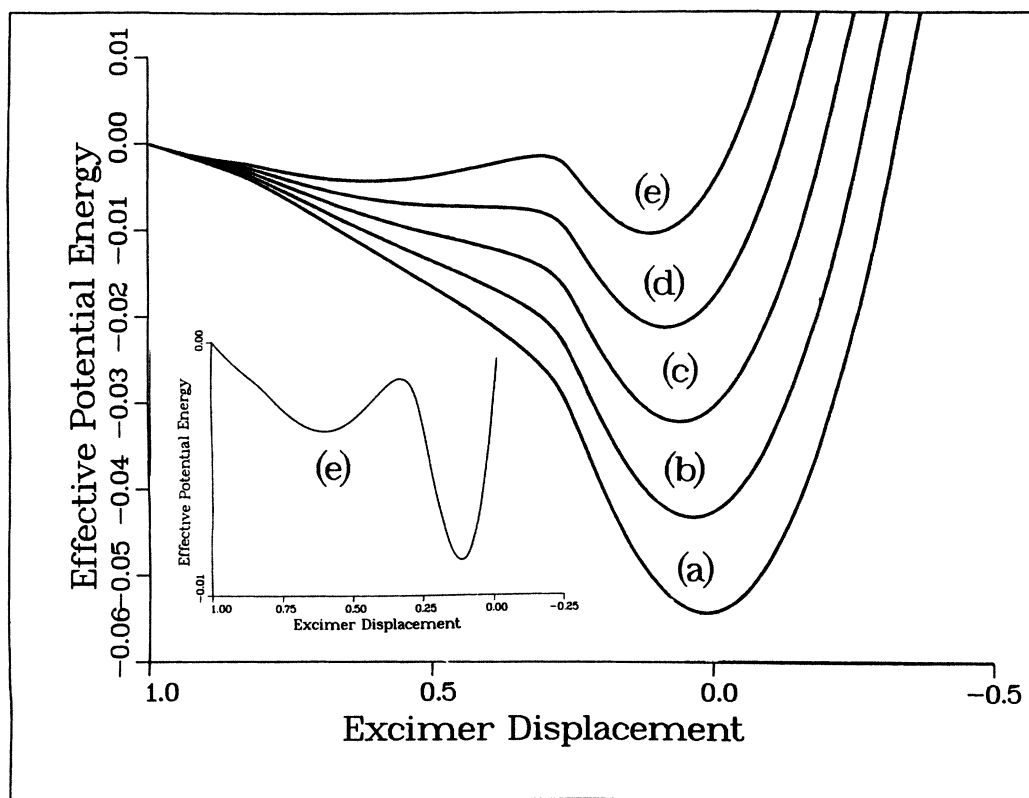


FIG. 5. The total potential, which is the sum of the nonlinear excimer potential and the effective lattice potential to which the excimer is subjected in the infinite  $t$  limit, shown, in arbitrary units, as a function of the excimer displacement  $\zeta$ , for five respective values of  $\omega_1/\omega_0$  in Fig. 2. The  $Y$  state is absent in cases (a)–(d) but appears in the form of the additional minimum in case (e). Note that, when the additional minimum appears, it does so at a value of  $\zeta$  removed by a finite amount from the location of the  $E$  state. The inset shows a magnified view of curve (e).

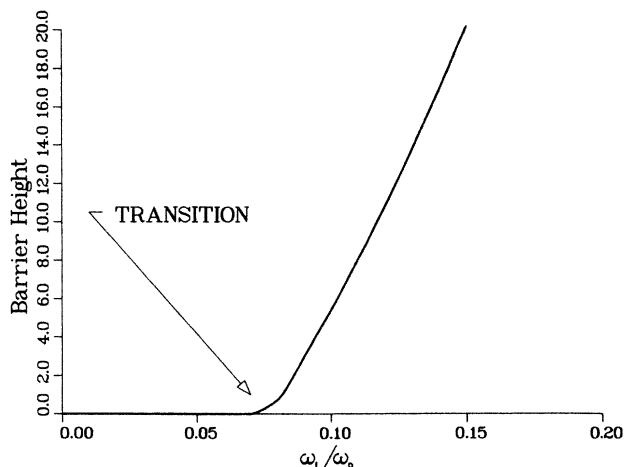


FIG. 6. The height of the barrier separating the  $Y$  state from the  $E$  state plotted as a function  $\omega_1/\omega_0$ . The barrier appears only when  $\omega_1/\omega_0$  exceeds the threshold value for the formation of the  $Y$  state and increases thereafter with an increase in  $\omega_1/\omega_0$ . Units of the barrier height are arbitrary.

#### IV. DISCUSSION

The  $Y$  state in excimer-forming crystals has always been an intriguing object of study in the physics of molecular solids. It has grown in importance as a result of careful recent experimentation<sup>13</sup> based on time-resolved techniques. However, theory has lagged considerably behind experiment in this field. The idea that the  $Y$  state probably arises from additional interactions of the excimer with the rest of the lattice which tend to oppose complete relaxation of the excimer has been around for some time.<sup>7-13,15</sup> However, a basic examination of the characteristics of a system which would or would not lead to  $Y$  states is lacking in the literature. Our analysis in the present paper attempts such an examination. The model we employ is the simple one<sup>16,17</sup> wherein the formation of an excimer is looked upon as the relaxation of an oscillator turned nonlinear by the absorption of light. The nonlinearity is required by the features of the observed spectra. In keeping with the prevalent idea, we explicitly include in our model interactions with the rest of the lattice which tend to oppose complete relaxation of the excimer. These are represented by the diagonal springs in Fig. 1 with spring constant  $k_1$  and frequency  $\omega_1$ .

The tool we employ for our analysis is the formalism developed in our earlier work.<sup>16</sup> The primary point of departure is Eq. (2.7) which describes the evolution of the excimer coordinate. Its time-dependent solutions describing the relaxation of the excimer indicate the possibility of the formation of a partially relaxed state. This possibility is suggested by a comparison of Fig. 2(a) to 2(b). The two differ in that the potential under which the excimer relaxes is nonlinear (as required by observed spectra) in the former but linear in the latter. The partially relaxed state which is merely suggested by Fig. 2 is made obvious by the time-independent analysis given in

Sec. III. That analysis is based on (3.3), which is an exact consequence of (2.7) and describes the dependence of the equilibrium (relaxed) value of the excimer coordinate on the characteristics of the system. The two sides of (3.3) describe, respectively, the nonlinear force which attempts to relax the excimer to the  $E$  state, and the linear force (with the "renormalized" force constant  $[1/\bar{\phi}(0)] - \omega_0^2$ ) exerted by the lattice which attempts to oppose that relaxation. The underlying picture, made quantitative here, is thus precisely that prevalent in the literature.<sup>7,15</sup> The new insights we obtain into the formation of the  $Y$  state are incorporated in Fig. 4 and in its result that can be seen in Fig. 3. The graphical solution to (3.3) provided by Fig. 4 shows clearly that the  $Y$  state will *not* arise every time a restoring force exerted by the rest of the lattice opposes the relaxation of the excimer. Indeed, for cases such as in curves (a) and (b) of Fig. 4 [or (a)-(d) of Fig. 5] *no Y state will be formed* despite such opposition. It is only when the magnitude of the opposing force and the nonlinearity parameters of the excimer potential combine suitably to provide multiple solutions for the equilibrium value of the excimer coordinate that a partially relaxed state will be formed in addition to the  $E$  state. Otherwise the effect of the lattice force will be simply to introduce a minor change in the location of the  $E$  state.

The reasons for the identification we make between the partially relaxed state which arises naturally from our analysis and the observed  $Y$  state in crystals such as  $\alpha$ -perylene are simple. Our analysis above has shown that the former is separated discontinuously from the fully relaxed state, that it does not arise in the absence of the hindering interactions, and that even when the latter are present, it arises only when the strength of those interactions exceeds a threshold value. These features appear to be highly similar to those observed in experiments on the  $Y$  state: The  $Y$  state is separated discontinuously from the  $E$  state, it is observed only in solids,<sup>22</sup> and some crystals exhibit it while others do not.

The limitations of our model include the fact that it is classical, it employs the simplest of lattices, and it does not include damping. Many of these shortcomings are planned to be removed in future work. However, the reason for the extreme simplicity of our model lies in the fact that our primary purpose in the present investigation is to arrive, in the most direct and conceptually economical manner, at the essence of the  $Y$  state.

Among future experiments that we believe are required in this area are those that would characterize crystals into a class which does and a class which does not exhibit  $Y$  states and those which would incorporate methods of converting crystals from one class into the other. Such methods might perhaps be similar (but employ quite different procedures) to pressure experiments<sup>23</sup> which have produced  $E$ -state excimers in crystals which do not ordinarily exhibit them. We hope that the work reported here will stimulate further observational investigations.

#### ACKNOWLEDGMENTS

One of us (V.M.K.) acknowledges the many helpful conversations he had with H. Port and H. C. Wolf on the

subject of excimers which sparked his interest in the field. We also thank H. C. Wolf for comments on the manuscript. This work was supported in part by the National Science Foundation under Grants No. INT-85-13058 and No. DMR-85-06438 and by the U.S. Department of Energy under Grant No. DE-FG04-86ER45272.

### APPENDIX

In order to derive expression (2.6) for the two-dimensional case, as expressed by the coupled differential equations (2.2) and (2.3), we proceed in the following manner. We write the corresponding set of equations for the relative variables  $\zeta_{m,n}$  and  $\psi_{m,n}$ , as defined in (2.4) and (2.5), respectively, and perform a discrete Fourier transform over the site indices  $m$  and  $n$ : The discrete Fourier transforms of  $\zeta_{m,n}$  and  $\psi_{m,n}$  are given by  $\zeta^{k,q}$  and  $\psi^{k,q}$ , where  $k$  and  $q$  are the reciprocal lattice vectors in

the  $x$  and  $y$  directions, respectively. After Laplace transforming the two coupled equations, it is straightforward to solve the resulting coupled algebraic equations for an expression relating the quantity  $\zeta^{k,q}$  to the Laplace transform of the nonlinear quantity  $k_0\zeta_{0,0}(t) - V'(\zeta_{0,0}(t))$ . Performing an inverse discrete Fourier transform, we obtain the expression

$$\begin{aligned} \tilde{\zeta}_{0,0}(\varepsilon) = & \tilde{\eta}_{0,0}(\varepsilon) \\ & + (1/M)\tilde{\phi}(\varepsilon) \left[ k_0\tilde{\zeta}_{0,0}(\varepsilon) - \int_0^\infty dt e^{-\varepsilon t} V'(\zeta(t)) \right] \end{aligned} \quad (\text{A1})$$

which, after an inverse Laplace transform, is simply (2.6). Since we always start with initial conditions such that the initial velocities and displacements are zero, the function  $\tilde{\eta}_{0,0}(\varepsilon)$  vanishes identically. The propagator  $\tilde{\phi}(\varepsilon)$  is given, for a two-dimensional system, by

$$\begin{aligned} \tilde{\phi}(\varepsilon) = & (2\pi)^{-2} \int_{-\pi}^{+\pi} dk dq 4 \sin^2(k/2) [\varepsilon^2 + \omega_q^2 + \omega_s^2 S(k,q)] \\ & \times \{ [\varepsilon^2 + \omega_q^2 + \omega_s^2 S(k,q)] [\varepsilon^2 + \omega_k^2 + \omega_c^2 S(k,q)] - \omega_{cs}^4 C^2(k,q) \}^{-1}, \end{aligned} \quad (\text{A2})$$

$$S(k,q) = 4 \sin^2[(k+q)/2] \sin^2[(k-q)/2], \quad (\text{A3})$$

$$C(k,q) = 4(\sin k)(\sin q), \quad (\text{A4})$$

and  $\omega_s^2 = \omega_1^2 \sin^2 \theta$ ,  $\omega_c^2 = \omega_1^2 \cos^2 \theta$ , and  $\omega_{cs}^2 = \omega_1^2 \sin \theta \cos \theta$ . The frequencies  $\omega_k$  and  $\omega_q$  are given by  $\omega_j = 2\omega_0 \sin(j/2)$ , where  $j$  is  $k$  or  $q$ , respectively, and the frequency  $\omega_1$  is given by  $(k_1/2M)^{1/2}$ .

One may follow the same procedure outlined above to obtain the expression for  $\tilde{\phi}(\varepsilon)$  in three dimensions. We have calculated this expression for the case that the diagonal spring constants are all  $k_1$ , and we have neglected interactions which are of longer range, i.e., the connections between opposite corners of a cube. We take  $j$ ,  $k$ , and  $q$  to be the reciprocal lattice vectors in the  $x$ ,  $y$ , and  $z$  directions, respectively, and define the angles of the diagonal connections as follows:  $\theta_{j,k}$  is the angle that the diagonal spring in the  $x$ - $y$  plane makes with the  $x$  axis,  $\theta_{k,q}$  is the angle that the diagonal spring in the  $y$ - $z$  plane makes with the  $y$  axis, and  $\theta_{q,j}$  is the angle that the diagonal spring in the  $x$ - $z$  plane makes with the  $z$  axis. The expression for  $\tilde{\phi}(\varepsilon)$  is then

$$\tilde{\phi}(\varepsilon) = (2\pi)^{-3} [D(\varepsilon)]^{-1} \int_{-\pi}^{+\pi} dj \int_{-\pi}^{+\pi} dk \int_{-\pi}^{+\pi} dq 4 \sin^2(k/2) [\Omega_k^2 \Omega_q^2 - \omega_{cs}^4(\theta_{k,q})], \quad (\text{A5})$$

where  $\Omega_k$  is given by

$$\Omega_k^2 = [\varepsilon^2 + \omega_k^2 + \omega_s^2(\theta_{k,q})S(k,q) + \omega_s^2(\theta_{j,k})S(j,k)] \quad (\text{A6})$$

for all  $k_j$ ,  $k$ , and  $q$ . The frequencies  $\omega_s^2(\theta_{j,k})$ ,  $\omega_c^2(\theta_{j,k})$ , and  $\omega_{cs}^2(\theta_{j,k})$  are the same as those in the two-dimensional expression, with the particular angle specified in parentheses, i.e.,  $\omega_s^2(\theta_{j,k}) = \omega_1^2 \sin^2(\theta_{j,k})$ . The function  $D(\varepsilon)$  is given by

$$\begin{aligned} D(\varepsilon) = & \Omega_j^2 \Omega_k^2 \Omega_q^2 - \Omega_j^2 \omega_{cs}^4(\theta_{j,k}) C^2(j,k) - \Omega_k^2 \omega_{cs}^4(\theta_{k,q}) C^2(k,q) - \Omega_q^2 \omega_{cs}^4(\theta_{q,j}) C^2(q,j) \\ & + 2\omega_{cs}^2(\theta_{j,k}) \omega_{cs}^2(\theta_{k,q}) \omega_{cs}^2(\theta_{q,j}) C(j,k) C(k,q) C(q,j). \end{aligned} \quad (\text{A7})$$

<sup>1</sup>J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley, London, 1970), Chap. 7.

<sup>2</sup>Th. Foerster, *Angew. Chem. Int. Ed. Engl.* **8**, 333 (1969).

<sup>3</sup>V. Yakhot, M. D. Cohen, and Z. Ludmer, *Adv. Theor. Chem.* **13**, 489 (1979).

<sup>4</sup>W. Kloepffer, H. Bauser, F. Dolezalek, and G. Naundorf, *Mol. Cryst. Liq. Cryst.* **16**, 229 (1972).

<sup>5</sup>Z. Lebovitz, S. Mansour, and A. Weinreb, *J. Chem. Phys.* **69**, 647 (1978).

<sup>6</sup>U. Mayer, H. Auweter, A. Braun, H. C. Wolf, and D. Schmid,

*Chem. Phys.* **59**, 449 (1981).

<sup>7</sup>J. Tanaka, *Bull. Chem. Soc. Jpn.* **36**, 1237 (1963).

<sup>8</sup>R. M. Hochstrasser, *Can. J. Chem.* **39**, 451 (1961); *J. Chem. Phys.* **40**, 2559 (1964).

<sup>9</sup>A. Matsui and H. Nishimura, *J. Phys. Soc. Jpn.* **51**, 1711 (1982); **49**, 657 (1980).

<sup>10</sup>T. Kobayashi, *J. Chem. Phys.* **69**, 3570 (1978).

<sup>11</sup>E. Von Freyendorf, J. Kinder, and M. E. Michel-Beyerle, *Chem. Phys.* **27**, 199 (1978).

<sup>12</sup>H. Auweter, D. Ramer, B. Kunze, and H. C. Wolf, *Chem.*



- Phys. Lett. **85**, 325 (1982).
- <sup>13</sup>B. Walker, H. Port, and H. C. Wolf, Chem. Phys. **92**, 177 (1985).
- <sup>14</sup>H. Port, R. Seyfang, and H. C. Wolf, J. Phys. (Paris) Colloq. **46**, C7-391 (1985).
- <sup>15</sup>M. D. Cohen, R. Haberkorn, E. Huler, Z. Ludmer, M. E. Michel-Beyerle, D. Rabinovich, R. Sharon, A. Warshel, and V. Yakhot, Chem. Phys. **27**, 211 (1978).
- <sup>16</sup>D. H. Dunlap and V. M. Kenkre, Chem. Phys. **105**, 51 (1986).
- <sup>17</sup>M. A. Collins and D. P. Craig, Chem. Phys. **54**, 305 (1981).
- <sup>18</sup>P. M. Morse, Phys. Rev. **34**, 57 (1929); R. Rydberg, Z. Phys. **73**, 376 (1931); C. L. Beckel and P. R. Findley, J. Chem. Phys. **73**, 3517 (1980).
- <sup>19</sup>M. K. Grover and R. J. Silbey, J. Chem. Phys. **52**, 2089 (1970).
- <sup>20</sup>T. H. Keil, Phys. Rev. **140**, A601 (1965); M. Lax, J. Chem. Phys. **20**, 1752 (1952).
- <sup>21</sup>See, e.g., H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971).
- <sup>22</sup>In all fairness it must be stated, however, that solutions which exhibit *E* states would be frozen at the temperatures at which *Y* states have been observed in solids.
- <sup>23</sup>A. Matsui, Abstracts of the Conference on Excimers in Solids, Ulm, 1985 (unpublished). See also P. F. Jones and M. Nicol, J. Chem. Phys. **48**, 5440 (1968); H. W. Offen, *ibid.* **44**, 699 (1965).