

Radiationless Transitions in Small Molecules: Interstate Cascading in Matrix-Isolated CN

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Radiationless relaxation following excitation of high levels of the $A^2\Pi$ manifold in CN is shown to proceed via an interstate cascading mechanism involving the $A^2\Pi$ and $X^2\Sigma$ vibrational levels. The direct vibrational relaxation within the $X^2\Sigma$ state is shown to be slower by at least 2–3 orders of magnitude. Experimental results and a theoretical discussion of these phenomena are presented.

Radiationless electronic transitions in molecular systems have been studied extensively in the past decade.¹ It is now well established that in large molecules this process is primarily intramolecular; in small molecules, where the density of accepting states is not sufficient to provide an effective quasicontinuum, coupling to medium modes plays an essential role. Firstly, it induces vibrational relaxation within the electronic manifolds involved, thus causing broadening of the vibronic levels and creating continuous spectrum. Secondly, it may provide modes which directly participate as accepting modes for the electronic energy. Both effects have been considered independently of each other by Nitzan and Jortner.² In this work it was assumed that intrastate vibrational relaxation is a much faster process than the interstate electronic transition, and an average rate for the transition between the two electronic states was calculated with this assumption. While this picture might be valid at high temperatures and/or for polyatomic small molecules, recent studies³ indicate that vibrational relaxation in matrix-isolated diatomic molecules is a relatively slow process, slower in some cases than the competing radiative relaxation or intermolecular energy transfer. Recent experimental studies by Bondybey⁴ indicated that the primary relaxation mechanism in the CN radical in Ne at 4°K excited to $A^2\Pi$ levels involves a cascading mechanism involving both $A^2\Pi$ and $X^2\Sigma$ levels as shown in Fig. 1. This would indeed be expected in the limit where medium-induced electronic transition is much faster than intrastate vibrational relaxation.

With this picture in mind it becomes interesting to check the proposed mechanism independently by directly monitoring the population of the ground-state levels. In particular, the above picture implies that the relaxation rates of levels 6" and 5" will greatly exceed those of levels 4" and 3", as the only pathway open for the latter

group is pure vibrational relaxation.

The population of the ground-state levels was studied by a sequential two-photon technique, in which one laser pulse excites one of the $A^2\Pi$ state levels, and a second laser probes the population of the desired ground-state level v'' after a variable time delay. This second laser is tuned to a wavelength connecting this v'' $X^2\Sigma^+$ level with some vibrational level of the higher-lying $B^2\Sigma$ state (typically $v' = v'' - 1$ or $v'' - 2$) and the $B^2\Sigma^+$ fluorescence intensity is monitored as a function of delay.

The time-resolved behavior of several levels obtained in this way is shown in Fig. 2 and the

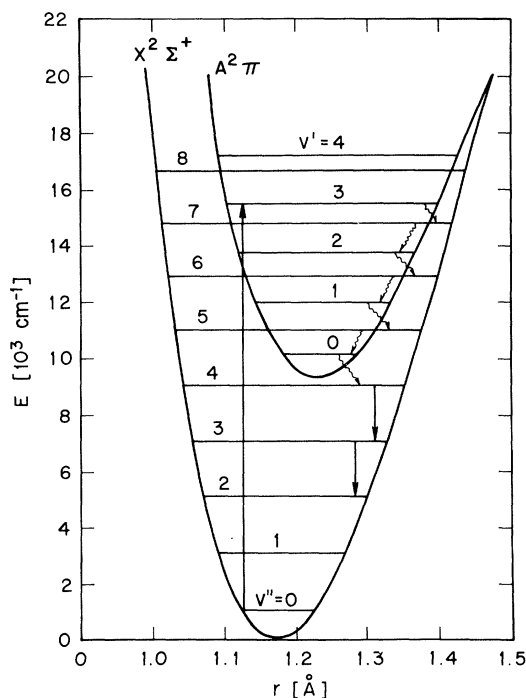
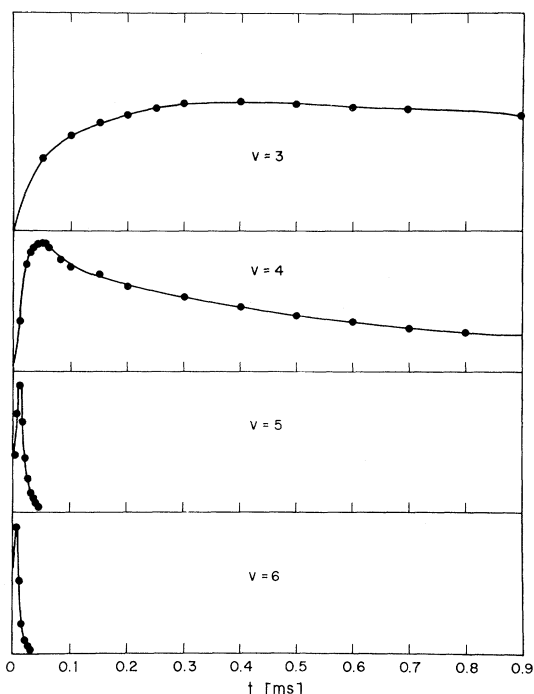


FIG. 1. CN potential curves and schematic of the observed relaxation processes. The wiggly arrows denote the radiationless relaxation; the solid vertical arrow shows the pump laser.

FIG. 2. Time-resolved behavior of the $X^2\Sigma^+$ levels.

numerical data are summarized in Table I. The results confirm that the $X^2\Sigma^+$ levels are efficiently populated following $A^2\Pi$ excitation, and show that the $v''=4$ and 3 relaxation rates are indeed several orders of magnitude slower than those of the higher levels. Comparison with similar diatomics indicates that the lifetimes of these levels may actually be close to radiative.

In considering the theoretical analysis of these data the following points should be kept in mind: (a) The molecular states are far enough apart in energy and the relevant phonon continua are practically mutually orthogonal (different continua correspond to states with different number of phonons) so that quantum mechanical interference effects are unimportant in the present relaxation process. (b) For the given molecular parameters the sequential nature of the relaxation process may be disregarded, i.e., the relaxation

TABLE I. Summary of the experimental relaxation data.

v' ($A^2\Pi$)	v'' ($X^2\Sigma^+$)	ΔE (cm^{-1})	τ (μs)
4	→	8	~0.01
3	←	8	7.5
3	→	7	0.09
2	←	7	5.0
2	→	6	0.67
1	←	6 ^a	
—		4 ^b	2800 ^c
—		3 ^b	5400 ^c

^aThe rates for this as well as for the $1'-5''$, $5''-0'$, and $0'-4'$ processes have not been accurately determined; the lifetimes are all in the range of 1–3 μs .

^bThese levels lie below $v=0 A^2\Pi$.

^cThese lifetimes are somewhat multiexponential as a result of site effects. The lifetimes given represent the predominant larger component.

rates are not affected by the finite lifetime of the accepting level. This can be shown using available expressions for sequential decay rates with the molecular parameters involved. Points (a) and (b) together imply that a classical kinetic scheme which invokes quantum mechanical transition rates between any two levels should be valid. (c) The coupling between vibronic levels which belong to the two electronic states X and A can be either vibronic, resulting from the breakdown of the Born-Oppenheimer approximation, or resulting from the residual spin-orbit interaction in the molecular Hamiltonian. In a diatomic molecule the molecular nuclear coordinate cannot provide a promoting mode for the coupling between two electronic states of different symmetry; the medium thus has to supply promoting modes in addition to being the source of accepting modes.

The standard zero-temperature expression for the multiphonon transition rate, in the approximation which takes into account only shifts in the normal modes origins, takes for our case the form (apart from irrelevant constants)⁵

$$W \sim C_{el} C_{FC} \exp(-S) \int_{-\infty}^{\infty} dt \exp(-i\Delta Et) \exp\left[\int d\omega f(\omega) e^{i\omega t}\right], \quad (1)$$

where C_{el} is the electronic coupling matrix element, C_{FC} is the molecular Franck-Condon overlap integral between the two vibrational states involved, ΔE is the energy gap between the two vibronic states, $\int d\omega$ is an integral over the phonon spectrum, and $f(\omega) = 1/2\Delta(\omega)g(\omega)$, where $g(\omega)$ is the phonon density and $\Delta(\omega)$ is the (dimensionless) origin shift. Finally, $S = \int f(\omega) d\omega$ can be obtained from spec-

tral data. Using the relation

$$\frac{\text{intensity of zero-phonon line}}{\text{total intensity}} \propto \exp(-S), \quad (2)$$

we estimate $S \sim 2$ for the $A-X$ transition. In writing Eq. (1) we have invoked the conventional Condon approximation in taking a product of overlap integrals involving the electronic states, the molecular vibrations and the lattice mode. Also we have disregarded (in case of vibronic coupling) the sum over different promoting modes.

To obtain an explicit expression for the rate W a model for the function $f(\omega)$ is needed. Particularly simple models which yield analytical results

are (1) Einstein,

$$f_1(\omega) = S(\omega - \omega_A);$$

(2) exponential,

$$f_2(\omega) = (S/n! \omega_A^{n+1}) \omega^n \exp(-\omega/\omega_A);$$

(3) Gaussian,⁶

$$f_3(\omega) = \frac{S}{\omega_A \sqrt{\pi}} \exp \left[- \left(\frac{\omega - \omega_M}{\omega_A} \right)^2 \right];$$

ω_A , n and ω_M are parameters that in principle can be fitted to spectral data. With these choices for $f(\omega)$ we obtain the following results: Model 1,

$$W \propto C_{el} C_{FC} \exp(-S) \frac{1}{\omega_A} \frac{S^\epsilon}{\epsilon!};$$

Model 2,

$$W \propto C_{el} C_{FC} \exp(-S) \frac{1}{\omega_A} \frac{\exp(-\epsilon)}{\epsilon} \sum_{l=0}^{\infty} \frac{S^l}{l! [l!(n+1)-l]!} \epsilon^{(n+1)l};$$

Model 3,

$$W \propto C_{el} C_{FC} \exp(-S) \frac{1}{\omega_A} \sum_{l=0}^{\infty} \frac{S^l}{l!} \left(\frac{\pi}{l} \right)^{1/2} \exp \left[- \frac{1}{l} \left(\epsilon - l \frac{\omega_M}{\omega_A} \right)^2 \right],$$

where $\epsilon = \Delta E / \omega_A$. Numerical results based on these models are displayed, together with the experimental results, in Fig. 3.

The experimental data represented by the solid line in Fig. 3 show, in qualitative agreement with theory, a steep rate dependence on the energy deficit. Quantitative agreement is, on the other hand, poor and all the models predict an even

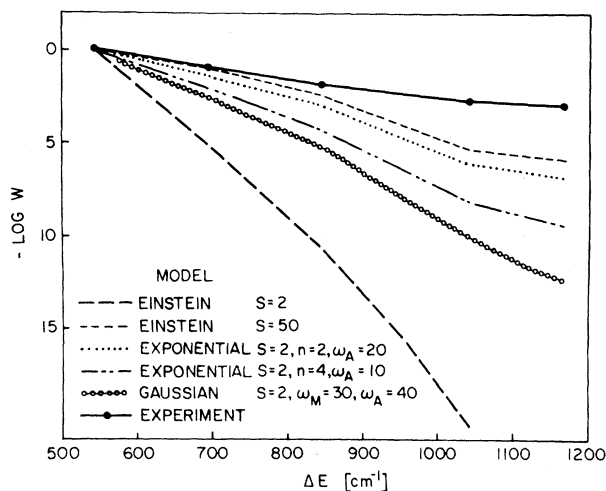


FIG. 3. Diagram of the experimental rates (solid plots) and those calculated using several theoretical models described in the text as a function of the energy gap.

stronger energy-gap dependence. Moreover, even for S as small as 2, multiphonon transitions account for more than half the sideband intensity and ω_A has to be chosen small to account for the observed line shape. This would further increase the dependence of W on ΔE , and the discrepancy is thus even bigger than shown in Fig. 3. This can be attributed to one or more of the following factors.

(a) Modification of the Franck-Condon factors by the matrix. The results in Fig. 3 use FC factors calculated for Morse oscillators with parameters chosen to fit matrix spectral data (but with gas-phase internuclear separation). Their comparison with matrix data shows that deviations of up to an order of magnitude may occur. Breakdown of the Condon approximation⁷ may account for further deviations.

(b) Vibrational state dependence of the parameters characterizing the molecule-lattice coupling. Above we assumed that the coupling parameters or equivalently the function $f(\omega)$ depend only on the electronic states and do not vary between particular pairs of vibronic levels. If S , ω_A , n , and ω_M become v dependent, more spectroscopic input data are needed for the theory to become useful.

(c) Quadratic coupling effects (e.g., phonon-

frequency changes during the electronic transition) as well as medium anharmonicity, increase the mean effective phonon frequency (due to the appearance of higher harmonics) and, therefore, are expected to moderate the calculated energy-gap dependence of the rate.⁸

(d) In principle slow processes can be masked by the occurrence of competing processes like infrared emission, pure vibrational relaxation, and energy transfer to other impurities. In the present case pure intrastate (infrared radiation or vibrational relaxation) relaxation was shown to be too slow to compete with the observed rates. The lack of concentration dependence of the rates also excludes energy transfer between different CN molecules.

In summary, we have established the importance of a process characterized by interstate cascading for the relaxation of diatomic guest molecules. The observed rates in CN qualitatively satisfy the energy-gap law but further studies

are needed to establish quantitative agreement.

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⁵See, e.g., R. Kubo and Y. Toyozawa, *Prog. Theor. Phys.* **13**, 160 (1955).

⁶We are grateful to J. Jortner for suggesting this model.

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First Operation of a Free-Electron Laser*

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A free-electron laser oscillator has been operated above threshold at a wavelength of 3.4 μm .

Ever since the first maser experiment in 1954, physicists have sought to develop a broadly tunable source of coherent radiation. Several ingenious techniques have been developed, of which the best example is the dye laser. Most of these devices have relied upon an atomic or a molecular active medium, and the wavelength and tuning range has therefore been limited by the details of atomic structure.

Several authors have realized that the constraints associated with atomic structure would not apply to a laser based on stimulated radiation by free

electrons.¹⁻⁵ Our research has focused on the interaction between radiation and an electron beam in a spatially periodic transverse magnetic field. Of the schemes which have been proposed, this approach appears the best suited to the generation of coherent radiation in the infrared, the visible, and the ultraviolet, and also has the potential for yielding very high average power. We have previously described the results of a measurement of the gain at 10.6 μm .⁶ In this Letter we report the first operation of a free-electron laser oscillator.

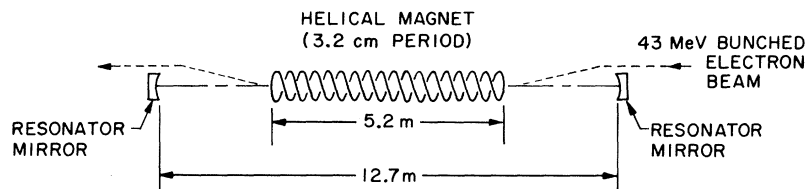


FIG. 1. Schematic diagram of the free-electron laser oscillator. (For more details see Ref. 6.)