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Optical Spectra of Molecules at Low Temperature

Intramolecular properties and environment determine the electronic spectra of matrix-isolated species.

Beat Meyer

The challenges of low-temperature spectroscopy were recognized by E. Wiedemann in 1888 and J. Dewar in 1895 (*1*). However, technical difficulties in the preparation of samples hampered work and progress for a long time. Vegard, for example, who conceived the first principles of matrix spectroscopy (*2*), had to travel from Oslo to the low-temperature laboratory in Leiden to test his ideas, and, until a few years ago, matrix work was restricted to those spectroscopists who had access to a good machine shop and leftover refrigerants from groups who had been investigating problems in physics or calorimetry. With the advent of air shipments of liquid helium through the United States and Europe, and with the development of very small refrigerators, this restriction has been eliminated, and the use of matrices for preparing and observing new and unstable species is now well established (*3*). The purpose of this article is to review and correlate the present knowledge of optical properties of various types of molecules in different matrices and to discuss problems encountered in the interpretation of spectra.

In order to retain characteristic spectra at low temperature, molecules must be embedded in weakly interacting solids. The three most common media are inert matrices, mixed crystals, and organic glasses. The field of low-temperature spectroscopy has grown so large that I shall not attempt here to present a full review (*4*). The spectroscopy of molecules in organic glasses at 77°K was pioneered by Kasha and McGlynn (*5*) and by Norman and Porter (*6*); Shpol'skii (*7*) discovered in 1954 that aromatic molecules in an appropriately selected hydrocarbon glass yield electronic spectra with sharp vibrational structure (*8*). Mixed molecular crystals were first investigated by Prikhotko and Skorobogatko (*9*) and by McClure (*10*), and newer work has been reviewed in conference reports (*11*). The rare gas matrix technique was developed by Pimentel and his co-workers (*12*), who use it to prepare radicals and other new molecules and to study their properties with infrared techniques. Pimentel and his students have made matrix isolation a field of broad interest. Work in this area has been reviewed by Milligan and Jacox (*3*). Electronic spectra in matrices were extensively studied by Bass and Broida (*13*), and by Robinson and McCarty (*14*) who discovered optical properties in a wide variety of molecules. Since the pioneer work of the late 1950's, more than 1000 reports on low-temperature spectra have appeared.

The present article deals with optical spectra of vapor-deposited molecules in inert matrices. Such matrices have several advantages. First, the inert matrix separates guest molecules from each other and reduces chemical and physical interaction between them. This makes it possible to store and to study radicals and other chemically reactive species and prevents migration of electronic excitation and spectral complications which arise in pure materials as a result of resonance coupling and other interactions between neighboring molecules. Second, spectra of vapor-deposited molecules in inert matrices consist of fewer lines than spectra in the gas phase, and the lines are sharper than those measured in liquid solution because of low thermal excitation. Third, solid matrices contain in a small volume a large number of molecules. Another advantage is that thermal effects can be studied over a large temperature range. A change from 4° to 20°K, for example, represents a fivefold increase in absolute temperature.

Sample Preparation

A good matrix is a weakly interacting solid with low lattice energy; thus intramolecular forces in the guest molecule are far larger than matrix-guest interactions. Spectra are thus predominantly characteristic of the molecular properties of the guest and show only secondary environmental perturbations. The electronic energy levels of the matrix should lie sufficiently high above the guest states so that the matrix is optically transparent and thermal depopulation of excited guest states into matrix exciton levels can be neglected. Rare gases with the lowest singlet exciton band in xenon at 68,000 reciprocal centimeters make ideal matrices for light molecules. However, in many cases, other molecules such as N_2, CH_4, CF_4, SF_6, C_6H_{12}, and C_4F_8 also make excellent matrices, particularly for emission studies. Substances such as SF_6, C_6H_{12}, CCl_4, and fluorocarbons are

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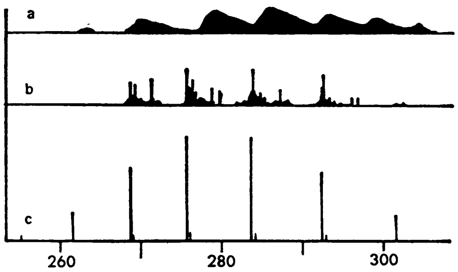

Fig. 1. Absorption spectrum of benzene: (a) liquid benzene at 300°K; (b) benzene crystal at 76°K; (c) benzene in nitrogen at 4°K.

useful for preparing rigid matrices at 76°K (*15*).

Matrix samples are prepared by vapor deposition of mixtures of the desired molecules with matrix gas. Stable gaseous molecules are normally mixed at a chosen ratio with the matrix gas and the mixture is then deposited as a molecular beam. In many cases it is advantageous to condense gases in bursts or flashes (*16*). Unstable molecules and weakly bound charge-transfer complexes may be formed in the depositing gas stream by direct reaction (*17, 18*) or in a microwave discharge (*19*). Stable solids, high-temperature molecules such as S_2, LiOH, and C_2, and atoms can be deposited from Knudsen furnaces (*20*). Radicals and other molecules may be best prepared in situ, by photolysis or diffusion-initiated reactions, or by a combination of both; such techniques have been perfected by Milligan and Jacox (*3*). In still other cases, the desired species can be made by reaction between matrix and guest. Carbon monoxide has proven to be an especially useful "reactive matrix" for the synthesis of HCO, ClCO, and FCO through reactions with the appropriate atomic precursor (*3*). In order to have mainly monomeric guest species, the ratio of matrix to guest must be large. Depending on how much dimer can be tolerated and on the relative size of guest and matrix, matrix-to-guest ratios are usually chosen between 100:1 and 10^5:1. In order to restrict diffusion during and after deposition, the target is normally cooled with liquid helium or hydrogen.

Absorption Spectra

The spectral properties of a sample depend on the electronic properties of the guest. Aromatic compounds normally give sharp spectra. Figure 1 shows the absorption spectrum of benzene at room temperature and in a nitrogen matrix (*21*) at 4°K. In the matrix the vibrational bands have a line width of less than 0.3 cm^{-1}. The lines have very weak satellites due to site effects and phonon interaction. Similar spectra are obtained for other aromatic compounds in rare gases, but the spectra are not always equally simple and sharp. Figure 2 shows the absorption spectrum of zinc phthalocyanine in argon, krypton, and xenon (*22*). The line widths in these matrices are less than 5 cm^{-1}, 10 cm^{-1}, and 20 cm^{-1}, respectively. If methane and sulfur hexafluoride matrices are used for zinc phthalocyanine, the spectra are equally good. The relative position of lines in different hosts is shifted by a fraction of a percent of the electronic transition energy. Since the spectra of the gas phases are complicated and the spectra of solutions are very broad, it usually cannot be determined which matrix gives the most gaslike transition energy. The fine structure in the inert matrices is much simpler than in hydrocarbon glasses, but the reason for the appearance of groups of doublets or triplets spaced by 10 to 50 cm^{-1} is not yet clear. On annealing, the intensity redistributes between the fine structure components.

Ferrocene (*23*) gives broader spectra, but the matrix data are still useful, because they are simpler than spectra in the gas phase and in solution. Of apparently 11 electronic transitions for ferrocene at room temperature, only five appear in a matrix at 20°K. The vibrational structure and line width can be used to correlate the transitions to the structure of the molecule. The absorption spectra of purine, adenine, thiazole, and other heterocyclic molecules have bandwidths of 200 cm^{-1} and more, but the bandwidths are sharper in the emission spectrum (*24, 25*).

Matrix spectra of diatomic and other small molecules are particularly simple because they have only one, or a few, vibrational modes. Therefore, matrices can be used to analyze complex electronic spectra, to confirm vibrational numbering, or to confirm the identity of new species. Recently reported examples include allowed and forbidden transitions in CuO, SeO_2, and a large series of diatomic high-temperature molecules (*26*).

Matrix Effects on Absorption

The line width of vibrational bands, which depends on the guest molecule, the transition, matrix material, and temperature, is 3 to 300 cm^{-1}. Atoms give the broadest lines, and Π-Π^* transitions of aromatics give the sharpest lines. The influence of the matrix is less clear. For example, the absorption spectrum of S_2 in xenon yields sharper lines than that of S_2 in argon. For emission spectra (*27*) the reverse is true. Another example in which line width has no apparent rationale is SO_2. The line width of SO_2 in nitrogen and krypton (*17*) is inordinately large, but the sharpest lines are observed in SF_6. The shift of transition energies between different solvents normally obeys the solvent heavy atom effect; that is, as the size of the solvent atom increases (argon < krypton < xenon), the spectra are increasingly shifted toward the red end of the spectrum. This effect was first observed and explained by Robinson and by McCarty and Robinson (*28*). The gas phase–matrix shift, however, is unpredictable. Often shifts in neon are the smallest. This is probably due

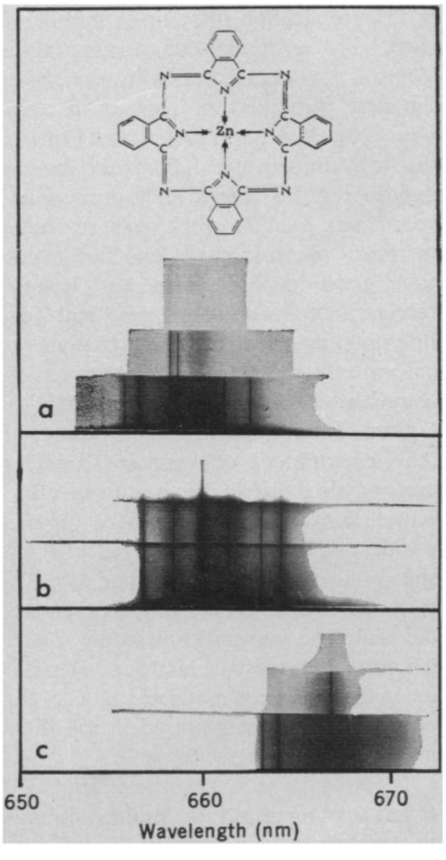

Fig. 2. Absorption spectrum of zinc phthalocyanine in various matrices at 20°K: (a) argon; (b) krypton; (c) xenon.

to the small polarizability of neon and its weak interaction with lattice and guest. Figure 3 shows that different vibrational modes undergo different shifts in different solvents.

The effect of environment on intensities is better understood. Allowed transitions are little changed, but spin-forbidden transitions are greatly enhanced by solvent heavy atoms. For example, the transition between the ground state and the first excited state

$$\tilde{a}\ {}^3B_1 \leftarrow X\ {}^1A_1$$

is not observed in 1 micromole of SO_2 in neon at 4°K, but in xenon the same amount of SO_2 yields a well-developed progression of vibrational bands and can be used for direct excitation of the triplet state (*18*). This intensity enhancement is due to increased spin-orbit coupling (*29*).

Nitric oxide constitutes an interesting example of another type of matrix effect. This gas has low-lying Rydberg states which in the gas phase interact strongly with the valence states. In matrices (*30*) the Rydberg states are broad and therefore too weak to be observed, and the perturbations of the Rydberg state on the valence states of the gas phase are suppressed. Thus the matrix spectrum shows only three electronic transitions between valence states with unperturbed vibrational spacing and intensity. Apparently, lattice interaction causes drastic broadening of lines. This suggests that changes in electron configuration, more than changes in internuclear distance, determine the extent of matrix perturbations. The correlation between line width and change of electron configuration is also demonstrated by the fact that transitions between well-shielded Π and Π* states in large organic molecules, with small changes in electron configuration, yield sharper lines and smaller shifts of transition energies than valence transitions in diatomic molecules, and that the unshielded atomic transitions all give the broadest lines. The line widths vary greatly, from 40 cm^{-1} for mercury in xenon at 4°K up to 1800 cm^{-1} for hydrogen in argon (*31*). The line width of multiplet transitions, for example, the transition

$${}^2P \leftarrow {}^2S$$

of alkali atoms, is also caused by random variations of lattice site distortion (*32*). A distortion of 0.1 angstrom could yield a line width of 300 cm^{-1}.

Fine Structure

Almost all spectra, on close inspection, are seen to exhibit fine structure. This can be due to intramolecular effects, multiple sites, or phonon interactions. In addition, very light diatomic molecules, for example OH and OD in neon, exhibit fine structure which has been interpreted as due to rotation coupled to the lattice (*33*).

Studies have been made of the atomic spectra (*34*) of many elements in rare gases, in SF_6, and even in ice. The degeneracy of atomic states and sublevels is removed in matrices by the low symmetry of lattice fields. Thus the number of transitions observed in matrices is almost always larger than the number observed in the gas phase. The low symmetry is caused by the different size of matrix and solute, and unoccupied neighboring sites (*32*). The identity of sublevels in copper has recently been confirmed by fluorescence experiments (*35*) which show that two lines of a triplet belong to the transition

$${}^2P_{3/2} \leftarrow {}^2S_{1/2}$$

and that the third belongs to

$${}^2P_{1/2} \leftarrow {}^2S_{1/2}$$

Temperature Dependence of Absorption

Chemical processes in matrices and optical properties of solutes are affected by matrix annealing and solute diffusion, both of which increase with temperature. Both processes occur to some extent during deposition. It is common practice to anneal samples in order to reduce light scattering and to induce transformation of unstable sites. Annealing can be used to discriminate between fine structure caused by multiple sites and intramolecular structure. This has been done in the case of alkali atoms, which show two sets of triplets with fine structure due to both effects (*36*). In the case of phthalocyanines (*22*), fine structure changes during annealing.

Depending on the size and mass of the solute and solvent, annealing can result in substantial diffusion. Diffusion is deliberately used for controlling chemical synthesis and reactions between radicals (*3*), but inadvertent diffusion results in dimers and aggregates which complicate the spectrum. Such effects have been qualitatively studied for Li, Na, K, and Rb in neon, argon, krypton, and xenon (*36*). However, there still exists considerable uncer-

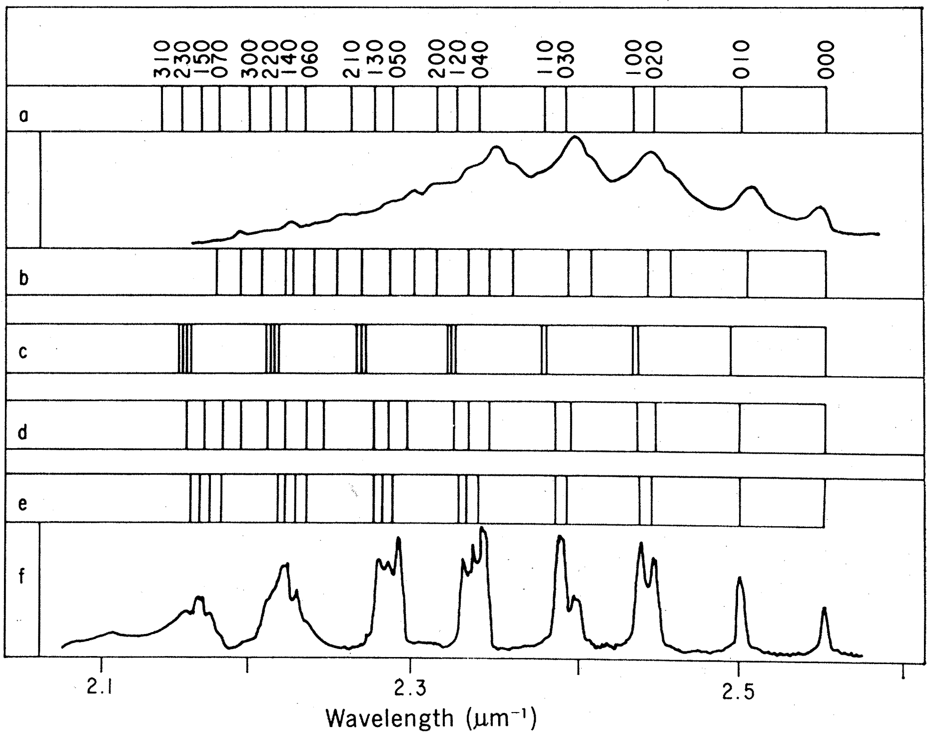

Fig. 3. Matrix effect on the emission of SO_2 at 20°K (*17, 18*): (a) gas phase; (b) emission spectrum in nitrogen and vibrational peaks; (c) argon; (d) xenon; (e) SF_6; and (f) emission spectrum in SF_6.

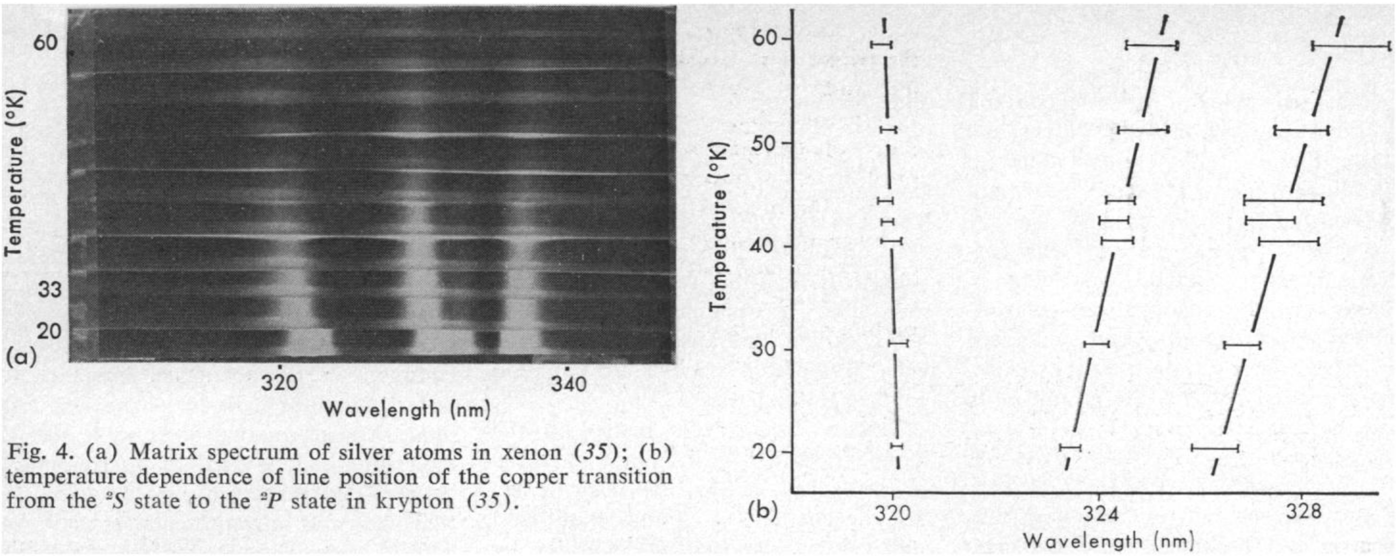

Fig. 4. (a) Matrix spectrum of silver atoms in xenon (*35*); (b) temperature dependence of line position of the copper transition from the ^2S state to the ^2P state in krypton (*35*).

tainty and contradiction about diffusion rates. One example (*37*) of the present state of affairs is that one group reports that lithium atoms diffuse in xenon at 4°K under all but the most careful conditions, while another group has reported observations of hydrogen atoms in argon at 30°K. With the present technology for temperature control, it will be much easier to establish activation energies for diffusion and chemical reactions, but so far no quantitative work has been reported.

Diffusion and annealing cause irreversible rearrangement in the solid. Figure 4a shows an example of a reversible temperature effect in the absorption spectrum of silver in xenon. Figure 4b is a plot of the reversible line shifts of copper in krypton (*35*). Similar effects are observed for other atoms in other solvents in the range below the temperature where diffusion occurs, that is, at approximately 0.4 of the matrix melting point. The line shift and hence the shift of transition energy is of the order of −1 to −6 cm^{-1} °K^{-1}, but the size and even the sign of the temperature coefficient is unpredictable. The line width is largest at the highest temperature, but it can either increase monotonously or go through a minimum. The splitting of sublevels of a given state increases with temperature. The line shift is due to density changes or phonon population, or both, but not even a qualitatively useful explanation has been advanced. This effect is greatest for atoms, smaller for diatomic molecules, and very small for large molecules.

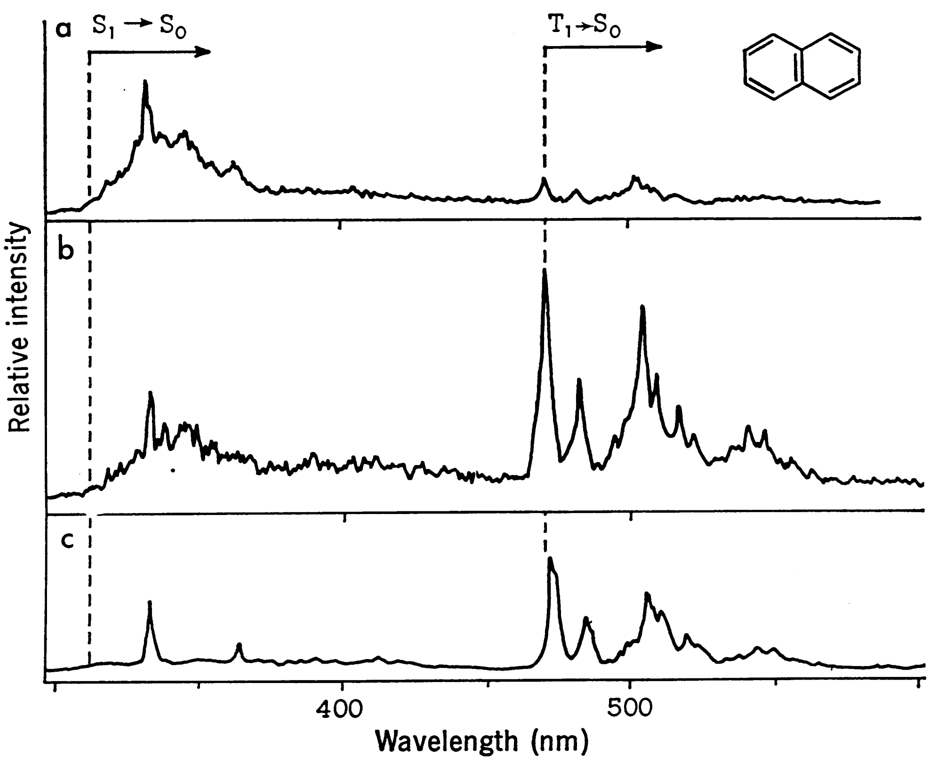

Fig. 5. Heavy atom solvent effect on fluorescence and phosphorescence of naphthalene at 20°K (*39*): (a) methane matrix; (b) argon; (c) krypton.

Emission Spectra

The emission of matrix-isolated molecules almost always originates from the lowest vibrational level of the emitting state, regardless of excitation frequency. The emitting state is usually the lowest excited electronic state of a given multiplicity, that is, normally the singlet S_1 or triplet T_1. This indicates that vibrational quenching is fast and that electronic relaxation to the first excited state is efficient (*4*). In the language of low-temperature spectroscopists, crossing between electronic states with the same multiplicity is called internal conversion (IC); radiationless transitions between singlet and triplet states are called intersystem crossing (ISC). Emission accompanying the transition

$$S_1 \rightarrow S_0$$

is fluorescence; emission accompanying the transition

$$T_1 \rightarrow S_0$$

is phosphorescence.

For almost all guests, phosphorescence is enhanced in the matrix and the lifetime for the transition from the T_1 state to the S_0 state is shortened. The strong enhancement of phosphorescence is the most characteristic

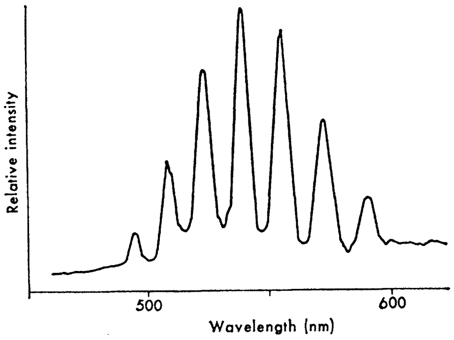

Fig. 6. Emission spectrum of GeS, excited at 310 nanometers, in krypton at 20°K. The transition is $\tilde{a}^3\Pi \rightarrow X^1\Sigma$ and corresponds to the Cameron bands of CO (*40*).

change in the emission of matrix-isolated molecules. It is due to intersystem crossing from S_1 to T_1. The amount of such spin-forbidden crossing is increased by the presence of heavy matrix atoms (*29*). An example of strengthened phosphorescence accompanied by weaker fluorescence due to intersystem crossing is shown in Fig. 5 for naphthalene in methane, argon, and krypton (*38*). In formaldehyde (*39*) a similar effect is observed, but it is less evident because fluorescence and phosphorescence overlap and one must use lifetime measurements to discriminate between the two. In many molecules the amount of matrix-induced intersystem crossing is so large that fluorescence is totally suppressed. This can even occur for molecules which, in the gas phase, exhibit only resonance fluorescence and no phosphorescence. Examples in point are the diatomic molecules SnS, SnO, GeO, and GeS, which in all rare gas matrices emit only from their previously unobserved lowest excited state $^3\Pi_1$ (*40*). Figure 6 shows the emission from $^3\Pi$, the Cameron bands, of GeS in krypton at 20°K. The total conversion of gas-phase resonance fluorescence into matrix-induced phosphorescence in the diatomic molecules [for example, GeS in Kr (Fig. 6)] as opposed to the subtle enhancement of intersystem crossing in naphthalene (Fig. 5) demonstrates that matrix effects on intramolecular guest properties depend on shielding of electron configurations.

The enhanced intersystem crossing in matrices makes it possible to use the high absorption coefficient of the bands of the allowed transition from S_0 to S_1 to excite strong emission from T_1, regardless of how strongly forbidden the emission is. This offers a unique and simple method for determining the location, lifetime, and other properties of the lowest triplet states of molecules. Knowledge of the properties of the triplet state is extremely useful for the study of reactions between atmospheric pollutants, biochemical reactions, photosynthesis, and the kinetics of all reactions involving excited states.

The vibrational structure of the emission spectra of large molecules is often complicated and not fully resolved because of the many vibrational modes of the ground state which can become terminal states of emission. The emission spectra of aromatic molecules are often "mirror images" (*41*) of the absorption spectra in sharpness, fine structure, and transition energy.

In some light diatomic molecules, for example, N_2 and O_2, vibrational excitation is not always quenched (*42*); that is, the vibrational lifetime is comparable to the electronic lifetime of the state. Vibrationally excited emission is observed for allowed and forbidden transitions. Electronic transitions are enhanced by the solvent heavy atom effect, but the intensity of emission from excited vibrational levels is largest in xenon and weakest in neon.

Radiationless Processes

We have seen that emission in matrices is influenced by radiationless processes, such as vibrational quenching, internal conversion, and intersystem crossing. These processes affect the spectral features, the intensity, and the lifetime. Consequently, many theories (*43, 44*) have been advanced for radiationless transitions in the gas phase and in the solid state for small, large, and intermediate molecules. The theories are based on stationary states or on time-dependent models, and they assume either purely intramolecular effects, intramolecular effects enhanced by the fact that the environment acts as an energy sink, or pure external perturbations (*43, 44*).

Table 1. Observed triplet decay times of benzene in various matrices. Numbers in parentheses in column 2 indicate the lifetimes of perdeuterated benzene.

Matrix	Decay time τ_P (sec)	Temperature (°K)	Reference
EPA*	7 (13)	77	(*46*)
1,4-Dioxane	5	77	(*47*)
CCl_4	0.66	77	(*47*)
Methane	15.8 (22)	4	(*44*)
Argon	16 (26)	4	(*44*)
Krypton	1	4	(*44*)
Xenon	0.07	4	(*44*)
Cyclohexane			(*48*)
Cubic	1.2 (9.2)	77	
Monoclinic	4.75 (13.9)	77	
Mixed	11.8 (15.6)	4	
C_6D_6	9.5	4	(*49*)
Borazine ($B_3N_3H_6$)	10.2 (12.5)	4	(*49*)
Ethanol	3.3	77	(*47*)

* Ether–isopentane–ethyl alcohol (5 : 5 : 2, by volume).

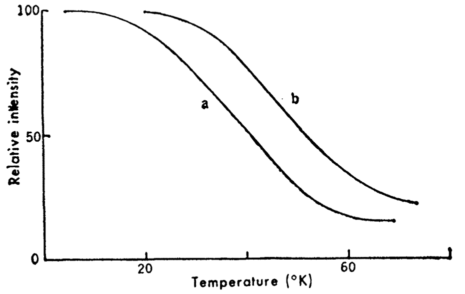

Fig. 7. Plot of intensity as a function of temperature for thiazole phosphorescence (a) in xenon and (b) in sulfur hexafluoride.

Most theories are based on observations of only a few aromatic molecules. For such large molecules in hydrocarbon matrices the number of parameters known and the number unknown are so large that many models can be fitted to the sparse data. In matrices the population of the T_1 state is enhanced, and the decay time of triplet states is shortened. Although free aromatic molecules are estimated to have radiative T_1 lifetimes of 20 seconds or more, the decay time in matrices is shortened to 1 second or less (*8*). Table 1 lists lifetimes, τ_P, for the $^3B_1$ state of benzene in various media. The lifetimes change from solvent to solvent, and differ for different types of guest sites. These variations have been established for benzene in cyclohexane, where τ_P is 1.2 seconds for the cubic site and 4.75 seconds for the monoclinic site. If different sites can coexist, plots of intensity as a function of decay time become complicated. In rigid matrices, phosphorescence decay times change less than 20 percent in the reversible temperature range between 4°K and 0.4 of the matrix melting point. Above the latter temperature, diffusion, annealing, and other irreversible processes become important.

Since the quantum yields are unknown and difficult to measure in solids, it is not clear how much of the shortening of the lifetime is due to radiationless decay and how much to changes in the oscillator strength, that is, to the relation between the solvent heavy atom effect and spin-orbit coupling. This could be decided if changes in absorption strength in different heavy atom solvents were observed, and the

Table 2. Phosphorescent lifetimes and relative quantum yield of SO_2 in various matrices (*4, 50*).

Matrix	Lifetime (± 1 msec)	Temperature (°K)	Relative intensities
Xe	5.2	20	100
Kr	8.4	20	60
Ar	9.0	20	40
Ne	17.5	4	15
CH_4	10.0	20	30
CD_4	9.6	4	30
SF_6	11.0	20	100
O_2	0.5	20	0.05
Pure SO_2	8.5	20	1

deduced relative oscillator strengths were compared with the data on decay time. Such work is difficult and has not yet been done. The data in Table 2 show qualitatively that both radiationless decay and oscillator strength can change. The weak emission and the short lifetime of the T_1 state in O_2 at 4°K is largely caused by quenching. In the series neon, argon, krypton, and xenon, the intensity increases proportionately to the lifetime decrease, an indication that the reduced lifetime is due to radiative processes, that is, a greater oscillator strength due to the solvent heavy atom effect.

Phosphorescence is usually excited by means of intersystem crossing from higher singlet states, or through the solvent exciton bands, rather than directly by absorption into the T_1 state, because the transition from the S_0 state to the T_1 state is weak. Lasers and other strong light sources allow direct excitation of triplet spectra, but optical properties of strongly irradiated solids become intensity-dependent because of delayed fluorescence caused by triplet-triplet annihilation. The intensity of indirectly excited phosphorescence is temperature-dependent (*17, 25*). The intensity change is greater than the change that would be expected from the change in the lifetime of the T_1 state. Figure 7 shows the relative phosphorescence intensity as a function of temperature for thiazole. The intensity changes are unusually large in all matrices. This must be due to the temperature dependence of the T_1 population mechanism, caused either by the temperature dependence of the intersystem crossing rate or by internal conversion from the S_1 state to the S_0 state. The effect is probably due to phonon-stimulated vibrational quenching.

Another process in which the effects are established but not yet fully understood involves the behavior of phosphorescence in the presence of a magnetic field. Phosphorescent decay of matrix-isolated molecules at high field strength is not a single exponential curve (*45*), because transfer of excitation between the different triplet sublevels is complex and cannot yet be explained.

Summary

Electronic spectroscopy of matrix-isolated molecules constitutes an efficient and convenient tool for the location of electronic states and for the determination of vibrational modes and other optical properties of guest molecules. Matrix spectra reflect primarily intramolecular characteristics. However, matrix interaction enhances intramolecular transitions to the T_1 state so that the properties of the lowest triplet state can be easily studied. Therefore, rare gas matrix systems constitute ideal and simple models for the investigation of solid state interactions. Finer details of electronic spectra, such as line shifts, line width and fine structure, intensity, polarization, and lifetime, have become better known and give insight into the structure of the solid, energy transport in the solid, and interactions with the guest. In addition, matrices will continue to serve the original purpose for which they were conceived, namely, the preparation and identification of new species.

Matrices are now so conveniently prepared that they can become part of routine experimental studies in chemistry, biology, and physics laboratories. However, despite the increasing wealth of data and the increasingly sophisticated experimental techniques, no aspect of matrix spectroscopy is adequately and thoroughly understood. There is still ample room for molecular spectroscopists and solid state physicists to discover new properties and phenomena correlated to radiationless transitions, spin-orbit coupling, energy migration, triplet-triplet annihilation, exciton fission, and, most important of all, diffusion in mixed solids.

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Enzymes Activated by Monovalent Cations

Patterns and predictions for these enzyme-catalyzed reactions are explored.

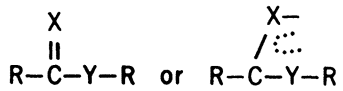
C. H. Suelter

The activation of certain enzyme-catalyzed reactions by monovalent cations is of interest to biologists and chemists, particularly since a potassium activation of the reaction catalyzed by pyruvate kinase was demonstrated (*1*). However, in contrast to the rather specific functions that may be assigned to certain divalent cations, the mode of action of the monovalent cations, $K+$ and $Na+$—particularly with respect to their ability to penetrate cell membranes, their affinities for active transport, and their potency for activating many enzymes (*2*)—has unfortunately remained obscure.

From an extensive compilation of enzymes requiring $K+$, Evans and Sorger (*3*) made the following generalizations. (i) A large number of enzymes catalyzing a wide variety of unrelated reactions are activated by monovalent cations. (ii) Those enzymes activated by $K+$ are also usually activated by $Rb+$ and $NH^{4}+$ but are activated little by $Na+$ and not at all by $Li+$. A few enzymes activated by $Na+$ are also activated by $Li+$, but they are activated much less or not at all by $K+$, $Rb+$, and NH_4+. (iii) The molar concentration of $K+$, $Rb+$, or NH_4+ required for maximum activity is high, having an activation constant K_A near $0.01M$ in most cases. (iv) The conformation of pyruvate kinase, an enzyme activated by monovalent cations, is affected by such cations. From these generalizations, Evans and Sorger (*3*) suggested that monovalent cations exert a role by maintaining a specific protein conformation necessary for optimum catalytic efficiency. In contrast, Melchior (*4*) and Lowenstein (*5*) proposed a complex of univalent cation and adenosine triphosphate based on results from model systems for a role of monovalent cations in phosphoryl transfer reactions. Yet not all enzymes activated by monovalent cations catalyze phosphoryl transfers.

If the monovalent cations participate in the catalysis, as implied by Melchior and Lowenstein, then the interaction of these cations with the substrate and enzyme forming a ternary complex for the catalytic event is consistent with (i) a conformational change of the protein, (ii) a hyperbolic saturation for cation activation as is normally observed (*6*), and (iii) a characteristic pattern of the reactions catalyzed by these enzymes.

In this article I now present my examination of the literature on these enzymes which culminated in the elaboration of a characteristic pattern for reactions activated by monovalent cations. The intermediates for one of the substrates in monovalent cation activated enzyme catalyzed reactions have the structure



$$R-\overset{\overset{X}{\|}}{C}-Y-R \quad \text{or} \quad R-\overset{\overset{X-}{/}}{C}-Y-R$$

where X is O, N, or C and where Y is O or N. The converse of this statement is not true.

Table 1 is a compilation of the enzymes activated by monovalent cations (*7*). For convenience, the enzymes are divided into two main classes; phosphoryl transfer (class K-P) and elimination reactions (class K-E). Class K-P is also subdivided into three subclasses, A, B, and C.

Reactions Activated by Monovalent Cations

Class K-P. The phosphorylation of the oxygen in the grouping $R-C(=X)-OH$, where X is O, NH, or CH_2, is catalyzed by the enzymes in class K-P. In many cases a phosphorylated compound is not the final product; however, a carboxyl oxygen is transferred to inorganic or pyrophosphate as phosphoryl transfer proceeds (*8*).

Subclass A of class K-P includes reactions in which X is oxygen, for example, carboxyl phosphorylation. In cases where monovalent cation activation has not been reported (*9*), it is possible that monovalent cations, particularly $NH+_4$, were present in assay solutions preventing the detection of activation.

Subclass B includes those reactions in

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