

SOME ASPECTS OF TRANSITIONS BETWEEN ELECTRONIC LEVELS

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The transitions between electronic levels of polyatomic molecules and their relationship to the photochemistry of such molecules has become of considerable interest during the past few years. Such transitions often occur without emission or absorption of radiation so that the state first formed by the absorption of radiation may not be the one most concerned with the resulting reaction kinetics.

In the present brief article we must of necessity limit the scope of the subject to be treated. Thus we will confine our attention to the gas phase¹. The problem in the liquid phase may be simpler in some cases than in the gas phase in the sense that vibration energy will be equilibrated with the surroundings before other processes can occur².

The terminology for the phenomena under discussion has not been the subject of international agreement³. We use the term *Internal Conversion* to refer to a non-radiative transition between states of the same multiplicity and *Intersystem Cross-over* to refer to a non-radiative transition between states of different multiplicity.

INTRODUCTION

It is now generally recognized that intersystem cross-overs and possibly internal conversions take place very frequently but data which permit precise calculations either of the magnitude of such processes or of the essential aspects of the mechanism are difficult to obtain and usually lacking.

When a molecule in the ground singlet state absorbs a photon the resulting excited molecule will also be in a singlet state and may do one of the following things: (a) fluoresce; (b) dissociate (possibly by passing through a triplet state); (c) undergo internal conversion to a lower (*i.e.* the ground) singlet state; (d) undergo an intersystem cross-over to a triplet state. Measurement of light emission may be used to determine the extent of (a). A detailed study of the kinetics of the system will in principle provide information about the extent of (b). Unless there exists some way of determining the amount of triplet state molecules formed, there is no way to distinguish clearly between (c) and (d)⁴ and no way exists to determine the sum of (c) and (d) except by difference between the number of photons absorbed and the sum of molecules which undergo (a) and (b). If a system with zero cross-over to the triplet state could be found, possibly the behaviour of the upper singlet state could be better studied^{5, 6}.

Evidence for (c) in most polyatomic molecules is far from conclusive. In

principle such conversions might occur as either kinetically first order or as kinetically second order processes. Under most experimental conditions ground state molecules with very large amounts of vibration energy which might be formed by internal conversion would be hard to detect. Fortunately internal conversions seem to be of negligible importance^{7, 8}.

Several methods may be used to determine the presence of triplet state molecules. These may be summarized briefly as follows: (a) character of the emission, *i.e.* the emission must be demonstrated clearly to be characteristic of the triplet state either by analysis of the spectrum or by determination of the mean lifetime of the emission; (b) electron spin resonance; (c) by energy transfer to other molecules on collision thus leading to a preferential emission or reaction from the triplet state of the colliding partner^{4, 9}. There are indirect and much less reliable methods available in some instances. For example, triplet states are at lower energies than the corresponding singlet states. This means frequently that dissociation from such states will require more activation energy than from corresponding singlet states.

Triplet state molecules may suffer several fates as follows: (a) dissociation, usually into radicals (see above); (b) light emission (often called phosphorescence) of longer mean life than that from the corresponding singlet state; (c) intersystem cross-over back to the excited singlet state² thus leading to a "delayed fluorescence" which has an apparent activation energy for its production; (d) intersystem cross-over to high vibration levels of the ground state in which case ultimately the energy would appear as thermal energy; (e) deactivation by collision of the second kind resulting in transfer of energy to other molecules; (f) interaction between two triplet state molecules which may result in dissociation of one of them¹⁰, perhaps by forming a molecule in a high vibration level of the ground state¹¹ or in raising one of the colliding partners back to a singlet state^{12, 13}.

It is the purpose of the present discussion to review the data for a few polyatomic molecules to determine both the extent of and the character of intersystem cross-overs and of internal conversions.

REVIEW OF DATA FOR A FEW MOLECULES

Ketene

Data relative to the primary photochemical process in ketene up to 1956 have been reviewed¹⁴. Since this molecule has been used many times as a source of methylene radicals¹⁵⁻¹⁸ and the resulting conclusions depend very much on whether or not intersystem cross-over occurs, it will pay to re-examine the data in the light of present concepts.

Quantum yields of carbon monoxide formation from ketene¹⁴ at temperatures below about 150° may be summarized as follows¹⁹:

At 3650 Å:

$$26^\circ 1/\Phi_{\text{CO}} = 13.0 + 37.3 \times 10^{-18} (K) \quad (1)$$

$$71^\circ = 7.2 + 13.44 \times 10^{-18} (K) \quad (2)$$

$$107^\circ = 4.4 + 8.54 \times 10^{-18} (K) \quad (3)$$

$$154^\circ = 3.9 + 3.4 \times 10^{-18} (K) \quad (4)$$

SOME ASPECTS OF TRANSITIONS BETWEEN ELECTRONIC LEVELS

where Φ_{CO} is the quantum yield of carbon monoxide formation and (K) is the concentration of ketene in molecules per millilitre. It is very doubtful whether an extrapolation to zero pressure predicts a behaviour which would correspond to actual behaviour under low pressure conditions. Thus G. B. Porter²⁰ has found apparent quantum yields of carbon monoxide at concentrations around 1.5×10^{-6} mole/l. (at 27° this is a pressure of about 0.028 mm) as follows: 0.54 (27°); 1.02 (70°); 1.73 (106°); 2.50 (154°).

At 3650 Å Porter²¹ has also found that oxygen very markedly reduces the photochemical dissociation of ketene into methylene and carbon monoxide but that there is a small reaction of "excited ketene" with oxygen to give products. This behaviour is reminiscent of the behaviour of triplet state molecules.

At 2700 Å one molecule of ketene dissociates per photon absorbed and this seems to be true also in the presence of oxygen although secondary reactions are changed by oxygen.

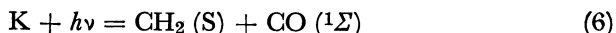
At 3130 Å the data are meagre^{22, 23} but such as they are they are intermediate between those at 2700 and those at 3650 Å. Quite probably results here will depend on the character of the monochromatic light used and conclusions in this wavelength region should be regarded with suspicion²⁴.

The absorption act for ketene may be represented at 3650 Å by



where K is a normal ketene molecule and 1K_n is a ketene molecule in the n 'th vibration level of the excited singlet state.

At 2700 Å the absorption act may be written



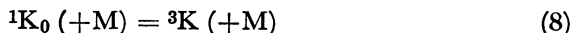
where $CH_2 (S)$ is a methylene radical in a singlet state and the carbon monoxide molecule is in its ground electronic state. For neither CH_2 nor CO can the amount of vibration energy be estimated.

The energy levels of methylene have been determined by Herzberg²⁵. The 1A_1 and ${}^3\Sigma_g^-$ states of methylene should lie close together and the ground state should be ${}^3\Sigma_g^-$.

It is now important to ascertain whether or not the 1K_n state of ketene passes over to the triplet state and then dissociates. The competing processes probably would be (7a), (7b), and (8):



(where 1K_0 is an upper state singlet ketene molecule with vibration energy equilibrated with the surroundings and D represents dissociation products)



(where 3K is a triplet ketene molecule). Not enough is known to decide whether collisions would be rate determining in (8) or not. The data¹⁹ which

form the basis for equations (1)–(4) were obtained at pressures from about 15 to about 200 mm. Even at the lower pressures in this range it is probable that vibration energy would be lost by 1K_n before events other than dissociation could occur. The quantum yields indicate that dissociation is relatively improbable unless shorter wavelengths than 3650 Å are used.

Thus we come to the conclusion that cross-over to the triplet state can occur if dissociation is not rapid but that no information exists as to whether the cross-over is aided by vibration energy in the ketene molecule.

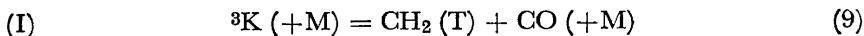
Murad²⁶ with the technique used in other connections^{9, 14} attempted to ascertain whether or not a triplet state of ketene is formed. In one experiment illumination of a mixture of ketene and biacetyl led to a strong emission of green by the biacetyl, thus giving presumptive evidence for a triplet state of ketene. However the walls of the vessel apparently became contaminated either with polymer or other reaction product and a thermal reaction subsequently occurred between ketene and biacetyl. Thus the experiment could not be repeated. Further work along these lines is planned.

The work of Porter²¹ and of Murad²⁶ strongly suggests that when ketene absorbs at 3650 Å many of the molecules, if not a majority of them, cross-over to the triplet state. The fates of these triplet molecules and the bearing they may have on work with methylene radicals may be mentioned. Suggestions can be made for subsequent work but it must be recognized that the data are at present in an unsatisfactory state.

Ketene has been used extensively as a source of methylene radicals^{15–18, 27, 28}. Methylene inserts itself into carbon–hydrogen bonds^{17, 27–31} and reacts with double bonds^{17, 18}. The evidence is reasonably conclusive that insertion into carbon–hydrogen bonds can occur only when methylene radicals are in singlet states. Addition to double bonds occurs with methylene radicals of either multiplicity, *i.e.*, there is no specificity to the reactions of the triplet state and there is to reactions of the singlet state¹⁷. Molecules which arise from the addition of methylene to the double bond of ketene might be more stable if $CH_2(T)$ is involved than if $CH_2(S)$ is involved because of the lower energy.

Evidence indicates that methylene does not change from singlet to triplet very rapidly although the rate of change increases with pressure of foreign gas³². The state in which the CH_2 is formed by and large determines the state in which it will undergo reaction under most experimental conditions.

The question now arises as to the fate of 3K molecules. The following possibilities may be considered:

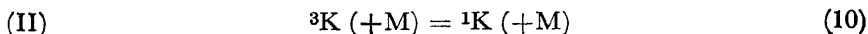


where $CH_2(T)$ is triplet state methylene. This would be in agreement with the work of Duncan and Cvetanovic³³ who studied the mercury-sensitized decomposition of ketene and of diazomethane.

If (9) is assumed for the dissociation at 3650 Å it has an activation energy of perhaps four or five kilocalories. However if triplet methylene is formed secondary reactions will differ from those at 2700 Å. Since the quantum yield of carbon monoxide formation is about two at short wavelengths singlet methylenes must react with ketene to give carbon monoxide. The other

SOME ASPECTS OF TRANSITIONS BETWEEN ELECTRONIC LEVELS

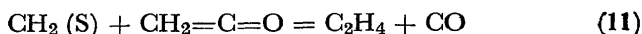
product is mainly ethylene but there is also some polymer¹⁹. Triplet methylenes should react readily with ketene as they do with other compounds which have double bonds. The products may not be solely ethylene and carbon monoxide. One would expect also methyl ketene, cyclopropanone, vinyl aldehyde, and perhaps polymer. Thus the carbon monoxide yield might be less than two and perhaps nearer one for each molecule of ketene which dissociates at the longer wavelengths. This matter needs further examination. As the temperature is raised the yield of CO per dissociating molecule would probably increase so that the observed activation energy may refer to a complex process



followed by reactions which could include dissociation of the singlet ketene. There is no evidence that singlet molecules such as ketene undergo internal conversion to the ground state^{7, 8} and no emission from ketene has so far been observed although attempts have been made to find it^{19, 24, 26}.

One must conclude, therefore, either that (10) is not very important or that there is a steady state between singlet and triplet ketene in which only a small amount of singlet ketene dissociates. Thus the main way of dissipating the absorbed energy at 3650 Å would be cross-over from ³K to the ground state.

With polychromatic light the quantum yield of carbon monoxide formation from ketene slightly exceeds unity³⁴⁻³⁶. Since the mechanism originally proposed by Norrish, Crone, and Saltmarsh³⁶ is now generally accepted, at least for short wavelengths, and this involves mainly the reaction



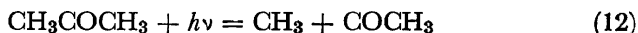
it must be concluded that polychromatic light gives a mixture of primary quantum yields. Moreover since the situation around 3100-3200 Å is intermediate between 2700 and 3700 Å it must also be concluded that a mixture of processes occurs with results which depend on what colour filters and what light sources are used. It would be quite surprising if workers in various laboratories would agree well with each other unless wavelengths below roughly 2800 Å were employed.

In concluding these remarks about ketene one must emphasize the following points: (*a*) more work with longer wavelengths is essential to establish beyond reasonable doubt the complete picture of the primary process; (*b*) almost certainly in the general wavelength region from about 3000 to about 3700 Å excited singlet molecules formed in the absorption act mainly cross over to the triplet state and such dissociation as takes place occurs with a small activation energy to give triplet methylenes; (*c*) since there are well-known differences in behaviour between singlet and triplet methylene radicals care must be used in interpreting results obtained at long wavelengths; (*d*) the apparent effect of collisions in enhancing the number of triplet methylenes may in reality be due to an effect in promoting cross-over of singlet ketene to triplet ketene rather than in promoting cross-over from singlet methylene to triplet methylene.

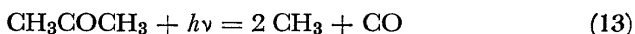
Acetone

The photochemistry of acetone has been investigated so extensively and reviewed so often^{14, 37} that little will be added in the present article. Nevertheless a brief statement in the light of current beliefs will be made.

It is now generally recognized that the primary process in acetone is



Norrish³⁸ originally proposed that part of the primary process could be written



but work with scavengers would indicate that there is a time interval between formation and dissociation of the acetyl radical¹⁴



The rate of (14) depends markedly on wavelength and on temperature but in the absence of scavengers the original statements by Norrish *et al.* are essentially correct under many experimental conditions. Thus recent work notwithstanding³⁹ there is good reason to believe that CH_3CO is formed initially with an amount of energy (probably mainly vibrational) dependent on wavelength³⁷. The wavelength dependence of the quantum yield of carbon monoxide and particularly of the $\text{CO}/\text{C}_2\text{H}_6$ ratio is difficult to understand in any other way⁴⁰.

The primary yield of (12) may only be calculated indirectly from the yields of known products and is subject to considerable inaccuracy^{10, 41}. This is true because foreign molecules used to remove radicals often also reduce the primary yield^{42, 43}.

At low temperature biacetyl is one of the principal products of acetone photolysis. Biacetyl is known to reduce the primary quantum yield in acetone^{44, 45}. Moreover yields from acetone are wavelength and temperature dependent. Conclusions about acetone must, therefore, be regarded with suspicion unless they are based on good monochromatic light and in the absence of certain foreign molecules.

Triplet state emission from acetone at room temperature is weak and singlet state emission is even weaker⁴⁶⁻⁴⁸. Furthermore both are excited at 3130 Å and neither is found at 2537 Å. The behaviour at intermediate wavelengths must show a transition from one extreme to the other⁴⁹. As the temperature is raised, the triplet state emission rapidly diminishes and the primary yield increases, presumably because the triplet state dissociates with a small activation energy⁴⁰. Furthermore biacetyl is not formed at high temperatures because the acetyl radical dissociates according to (14).

At 2537 Å at all temperatures the primary yield is probably unity and there is no light emission¹¹. At 3130 Å it is difficult to use the data to ascertain how many molecules undergo an intersystem cross-over from the triplet to the ground state but the extent of the cross-over from the excited singlet to the triplet state may be estimated from the maximum triplet emission from

biacetyl in acetone-biacetyl mixtures^{45, 50}. Since about 0.15 of triplet state biacetyl molecules emit radiation, the fraction of acetone molecules which cross-over to the triplet state is about 0.2. If one adds to this the primary yield from the singlet state (*e.g.* the yield when biacetyl is present) one finds that some sixty-six per cent and perhaps as much as ninety-two per cent of the singlet state molecules are accounted for. It is very difficult at present to say whether it is necessary to postulate some other process to account for the remainder or whether the errors are so large that the total fraction accounted for may in fact be unity.

Biacetyl

In biacetyl the situation is more definite, largely because absorption at 4358 and at 4047 Å leads only to negligible dissociation at room temperature. Such dissociation as there is results almost entirely from collisions between triplet state molecules⁵¹.

At 3650 Å at low pressures biacetyl dissociates but at higher pressures rapid loss of vibration energy by collision prevents dissociation. Since the dissociation as far as is known is entirely into radicals, quite possibly the cross-over from singlet to triplet leads to dissociation if the crossing molecule possesses enough vibration energy. The triplet state with equilibrated vibration energy dissociates with an activation energy of about 15 kcal⁵¹.

Almy and his co-workers have determined the triplet emission yield from biacetyl at room temperature to be about 0.15 at 4358, at 4047, and, at sufficiently high pressures, also at 3650 Å. The work of G. B. Porter⁵² and of Bäckström⁵³ indicates that all absorbing biacetyl molecules cross to the triplet state except the fraction 0.0025 which emit from the singlet state. Thus the cross-over is essentially quantitative if the vibration energy in the excited singlet state is low. At 3650 if the pressure is more than 10 to 20 mm loss of vibration energy is more rapid than either cross-over or dissociation. This must be true since Okabe⁴⁸ found the ratio of singlet to triplet emission to be independent of both absorbed wavelength and of pressure at constant temperature.

One may conclude that dissociation occurs in less than 10^{-6} to 10^{-7} sec at 3650 Å. At this wavelength at low pressures the mean life of the singlet state will be determined by the rate of dissociation. Since singlet and triplet emissions from biacetyl are not self quenched, the mean life of the singlet state at ordinary pressures will be determined by the radiative process and by intersystem cross-over with the latter predominant. This life has not been measured precisely but it is known to be less than 8×10^{-6} sec⁴⁷.

One may now raise the question as to whether excited biacetyl molecules formed at 3650 Å pass through the triplet state en route to dissociation. It is almost certain that any cross-over process will be aided by appreciable amounts of vibrational energy†. If this is so singlet molecules formed at 3650 Å should cross over much more rapidly than those formed at longer wavelengths. The activation energy for dissociation of the triplet state is about 15 kcal⁵¹ and this added to the electronic energy of the triplet state (about 55 kcal) corresponds to about 70 kcal or roughly equivalent to photons

† The authors wish to thank Professor F. A. Matsen for a helpful discussion of this point.

at 4000 Å (3.1 eV). Hence triplet state molecules which have the full 3.4 eV of energy corresponding to 3650 Å should dissociate rapidly.

Methyl ethyl ketone (2-butanone) at room temperature dissociates mainly to give ethyl and acetyl radicals, but roughly 12 per cent of the primary process goes to methyl and propionyl radicals¹⁴. Emission is weak and identical with that of biacetyl¹⁴. The primary quantum yield has not been determined but must be over 0.8 at room temperature at 3130 Å and probably increases both with temperature and with decrease in wavelength. At 3130 Å cross-over to the triplet state should be appreciable. The primary yield should be unity at 2537 Å as it is for acetone and for 3-pentanone (see below).

Weir⁵⁴ has recently confirmed earlier work that the primary yield in diethyl ketone (3-pentanone) is very close to unity even at room temperature at 3130 Å. Nevertheless, by addition of biacetyl he showed that there is an appreciable amount of triplet state formed. In this instance the triplet state dissociates rather than crossing over to the ground state.

Other Ketones

When one reaches ketones with carbon atoms gamma to the carbonyl group, *e.g.* methyl *n*-propyl ketone (2-pentanone) and ones with longer radicals, the picture seems to change abruptly. These ketones can undergo what has come to be called a Norrish Type II reaction⁵⁵:



As Norrish and his co-workers showed this reaction does not proceed *via* free radicals. It was suggested⁵⁶ that it almost certainly results from an internal six-membered ring formed by hydrogen bonding of a gamma hydrogen to the carbonyl oxygen. This has since been shown to be the probable course of the reaction⁵⁷ since the enol form of acetone has now been shown to be formed⁵⁸.

The Norrish Type II reaction probably occurs from the singlet state⁵⁹ although Ausloos has reached a different conclusion⁶⁰. The inhibiting effect of oxygen is less than would be expected if the triplet state were involved.

The final proof that triplet state molecules are not formed when a Norrish Type II reaction can occur has not been fully proved but the data suggest⁶¹ that this is the case at least at room temperature at 3130 Å. As the temperature is raised dissociation into radicals becomes relatively more important. By implication one could draw the conclusion that cross-over to the triplet state occurs more easily from high than from low vibration levels. The triplet state would then dissociate with a small activation energy to give radicals, a phenomenon already mentioned above.

Benzene

Much has been written recently about benzene and other aromatic hydrocarbons and no attempt will be made to give a complete summary of this work. Biacetyl (see above) and benzene⁶² in the gas phase provide two examples of molecules for which the data are reasonably good and which indicate that probably all molecules which do not emit from the

first excited singlet state cross over to the triplet state. By implication all processes whether first or second order which destroy molecules in the first excited singlet state, except light emission, lead to production of triplet state molecules. There are probably many other examples but, as we shall see, the data are not accurate enough to permit this conclusion to be quantitative.

The zero-zero band for the transition ${}^1A_{1g}^- \rightarrow {}^1B_{2u}^-$ is placed at about 2625 Å (4.72 eV)⁶³ and the electronic term for the ${}^1B_{2u}^-$ state is placed about 4.89 eV above that of the ground state⁶⁴. The triplet state ${}^3B_{1u}^+$ corresponding to this singlet state is stated to have an electronic term of 3.66 eV⁶⁴. Emission from it has been observed only at low temperatures in glassy matrices^{65, 66}. In the presence of dissolved para-magnetic gases such as oxygen absorption leading to its direct formation may occur⁶⁶.

Many studies have been made of the fluorescence of benzene⁶⁷. It is only slightly self quenched^{62, 67}, the extent possibly depending on the exciting wavelength even at moderate pressures⁶⁸. If this is so there must be a process leading to disappearance of the ${}^1B_{2u}^-$ state dependent on vibration energy. At pressures over about 10 mm the emission spectrum is independent, as one would expect, of the exciting wavelength but resonance emission becomes more pronounced at lower pressures.

Emission by benzene is excited at 2654, at 2537, and at 2480 Å but it is certainly very weak⁶⁹ when benzene is exposed to a wavelength of 2345 Å. The emission efficiency at the longer wavelengths is greater for C_6D_6 than for C_6H_6 . Leach and Migirdicyan⁷⁰ have found evidence of hexatriene formation at low temperatures in the glassy state. Hexatriene would have a short life. At shorter wavelengths cuprene and some hydrogen are formed⁷¹ but at 2345 Å no gas volatile at liquid nitrogen temperatures is formed⁶⁹.

The behaviour of benzene vapour at 2345 Å is interesting. The absence of emission at 2345 either when the benzene pressure is high or when several centimetres of cyclohexane are added indicates that some other process occurs at this wavelength. Loss of vibration energy by collision does not seem to suffice to permit radiation.

Comparison of C_6D_6 and C_6H_6 indicates strongly that the amount of vibration energy affects the rate of cross-over since the two molecules increasingly resemble each other as the temperature is raised⁶⁸. At room temperature the emission efficiency of C_6D_6 is greater than that of C_6H_6 when both are excited at 2654 and at 2537 Å.

The data do not provide conclusive evidence of what occurs but a few possibilities will be suggested: (i) The ${}^1B_{1u}^+$ state of benzene has an electronic term of about 6.14 eV⁶⁴. Just possibly absorption at 2345 Å is mainly to this level but this is doubtful. (ii) Two other triplet states of benzene, ${}^3B_{2u}^-$ and ${}^3E_{1u}^+$, must lie in this general energy region⁶⁴. Cross-over to either of these from ${}^1B_{2u}^-$ vibrationally excited might occur through perturbations caused by collisions. (iii) At the pressures used the cross-over must occur in less than about 10^{-6} sec if it is to compete with loss of vibration energy.

The mean life of the singlet state of benzene as measured experimentally (about 0.8×10^{-6} sec)⁷² agrees excellently with the radiative mean life calculated from the absorption coefficients⁷². However, as previously

pointed out this agreement is fortuitous⁶² since the disappearance of the singlet state is due mainly to processes other than radiation. It is possible that if a molecule in the ${}^1B_{2u}$ state is formed with sufficient vibration energy the cross-over will occur before enough vibration energy is lost to make radiation competitive with cross-over. A more careful study of emission efficiency as a function of wavelength and of pressure is necessary before this explanation can be discarded.

Insufficient evidence exists to permit a choice to be made between these possibilities.

Finally brief mention must be made to the ultimate fate of the triplet state, ${}^3B_{1u}$, molecules. In the glassy state they have lives of about 20 sec⁷³. In the gas phase they almost certainly have lifetimes less than 10^{-4} sec⁶². They may react with oxygen with a rather low quantum yield⁶⁹. However the triplet state may cross back to the singlet state by a process with an activation energy. Emission efficiency from the singlet state seems not to increase with increase in temperature⁶⁸. The mean life of the singlet state emission as a function of temperature should be determined carefully to ascertain whether or not there is any "delayed fluorescence".

The problem of the kinetic treatment of cross-over problems has been recently examined and some of the criteria which may be used to decide between various possibilities have been indicated⁷⁴.

Few measurements of "absolute" emission yields of gases are available. The classical work of Almy and Gillette⁵⁰ has often been used as a standard. These authors place the emission yield of biacetyl vapour (now identified as the triplet emission) as 0.15 ± 0.03 at room temperature at 4358 and at 4047 Å. At 3650 Å the yield is lower but approaches 0.15 as the pressure is increased. There is no reason to doubt either the accuracy of this measurement or the limit of error placed on the value by the authors themselves. Nevertheless the importance of this field is such that the emission yield of biacetyl should be remeasured and if possible the probable limits of error reduced. This should be possible with modern techniques.

If one accepts the yield of Almy and Gillette and refers to the data on benzene⁶², one example will suffice to show the need for more accuracy. At 20 mm pressure Ishikawa found the absolute fluorescence yield of benzene (using the biacetyl value as a standard) to be 0.22. In the presence of biacetyl the benzene-sensitized emission yield of the triplet state of biacetyl was 0.12. Since 0.15 is the fraction of triplet state biacetyl molecules which emit⁵⁰, one concludes that the yield of the triplet state of biacetyl sensitized by benzene is $1.00 \times 0.12/0.15 = 0.08$, in satisfactory agreement with $1.00 - 0.22 = 0.78$, the fraction of the absorbing benzene molecules which do not fluoresce. Hence the conclusion was drawn that all absorbing molecules either fluoresce or cross-over to the triplet state. However in view of the limits of error placed on their own work by Almy and Gillette one must conclude (without assuming any additional errors in the work of Ishikawa) that the fluorescence yield is in fact 0.22 ± 0.044 and the sensitized biacetyl emission yield 0.12 ± 0.024 . Thus the fraction of absorbing benzene molecules which cross over to the triplet state may be as low as 0.64 and as high as 0.82. Quite obviously the sum

$$Q_f + 0.9975 \times Q_s/Q_B$$

SOME ASPECTS OF TRANSITIONS BETWEEN ELECTRONIC LEVELS

may not exceed unity. (Q_f is the emission efficiency of the singlet state of benzene; 0.9975 is the fraction of the absorbing biacetyl molecules (in pure biacetyl) which do not emit from the singlet state; Q_s is the emission efficiency of biacetyl from the triplet state; Q_b is the efficiency of the benzene sensitized emission of biacetyl.) The lower limit is determined by Q_b and the upper limit by Q_f .

More quantitative absolute data with highly monochromatic light at a series of pressures are essential. Quite obviously such data will not be easy to obtain, particularly in view of the very great effect of trace impurities.

The authors wish to express appreciation to Mr W. A. Mulac of the Argonne National Laboratory for help in performing some of the experiments with benzene and to Dr M. S. Matheson also of Argonne for many helpful discussions.

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