ENERGY TRANSFER BETWEEN BIACETYL AND IODINE IN THE GAS PHASE

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Summary

Quenching of biacetyl phosphorescence by molecular iodine is very efficient. The energy transfer rate constant ($(7.7 \pm 0.5) \times 10^6$ Torr^{-1} s^{-1}) indicates that biacetyl is deactivated on every collision. Dissociation of iodine is indicated as well as population of the $B^3\Pi_{0u^+}$ state. A broad emission centred around 580 nm appears in the mixture. The assignment to the B state requires a non-statistical distribution of the vibrational level population.

1. Introduction

The lowest excited state $T_1(^3A_u)$ of biacetyl is remarkably stable. Under collision-free conditions its lifetime, approximately 1.8 ms, is governed by intersystem crossing to the ground state $S_0(^1A_g)$ [1, 2]. The phosphorescence lifetime and quantum yield are independent of pressure up to at least 40 Torr [1 - 3]. Biacetyl is one of the few molecules that phosphoresce strongly even in liquid solution at room temperature. Energy transfer experiments are also indicative of the considerable stability of T_1. Phosphorescence quenching is inefficient in cases where the lowest triplet state of the collision partner lies at a higher energy than the vibrational zero point energy $E(T_1)$ of biacetyl. Examples include sulphur dioxide, cyclohexane [3], acetone, methyl chloride and isopropyl alcohol [4], various alkylamines [5], some aliphatic alcohols and iodides [6] and *cis*- and *trans*-2-pentene [7]. Higher quenching efficiencies have been reported for molecules with low-lying triplet states, *e.g. cis*- and *trans*-1,3-pentadiene [7], azomethane and azoethane [8] and anthracene [9], and for the paramagnetic molecules nitric oxide [8, 10] and oxygen [1, 3, 8, 10]. Even so, quenching rate constants are found to be considerably smaller than those predicted from the kinetic theory of gases (gas kinetic rate constants). For example, about 300 collisions are required in the case of oxygen [8].
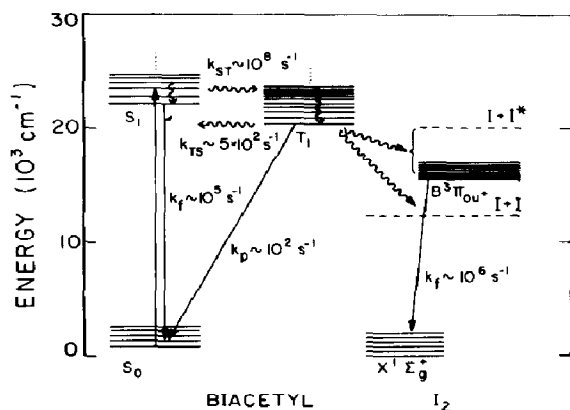
Fig. 1. A partial energy level diagram showing some low-lying electronic states of iodine and biacetyl. The energies are taken from ref. 12 (iodine) and ref. 13 (biacetyl). Several repulsive states of iodine, correlating with two ground state iodine atoms are not included. The approximate rate constants for radiative ($\longrightarrow$) and non-radiative ($\leadsto$) transitions are shown.

A notable exception is the high quenching efficiency of iodine molecules, already noted over 40 years ago [11]. A rate constant was not reported, but it was estimated to be 50 - 100 times larger than that of oxygen, i.e. energy transfer on almost every collision. Inspection of the energy level diagram (part of which is reproduced in Fig. 1) led to the tentative attribution of the high efficiency to the spin-allowed energy transfer from T_1 to the $B^3\Pi_{0u^+}$ state of iodine:

$$BA(T_1) + I_2(X) \xrightarrow{k_1} BA(S_0) + I_2(B) \qquad \Delta E = 4760 \text{ cm}^{-1} \qquad (1)$$
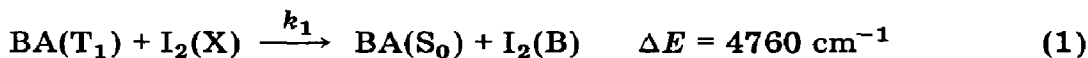
where the excess energy can be dissipated as vibrational or translational energy. In this work we present a more detailed study of the process, in which we find that the energy transfer rate constant is indeed essentially gas kinetic. Our data are an indication that process (1) does take place but that it is probably not the major channel. Other routes, such as dissociative energy transfer, are important.

Optical excitation of biacetyl at the lowest spin-allowed transition initially results in the population of the first excited singlet ^1A_u state. Rapid intersystem crossing leads to the formation of the triplet state. The nature and dynamics of biacetyl emission under collision-free conditions and the effect of collisions have been extensively discussed [14, 15]. For the present work the important feature is that collisions lead rapidly to the loss of about 2200 cm^{-1} of vibrational energy per collision from the population of the thermalized triplet [14]. It follows that in the electronically excited biacetyl–iodine system the only important donating state is the thermalized triplet.

Equation (1) represents electronic excitation of a diatomic molecule by energy transfer from a polyatomic molecule. To our knowledge such processes have not been extensively studied. In the present case the well-known

B—X transition of iodine may be used to follow the kinetics and the energy branching ratio associated with process (1). In view of the large number (30) of vibrational modes in biacetyl, a statistical distribution of the excess energy would lead to preferential population of low-lying vibrational levels of the B state. If this situation holds, we expect to observe a simple emission spectrum consisting mostly of the $v' = 0$ progression only. At the other extreme, if a "sudden" electronic energy transfer takes place, *i.e.* if all the vibrational degrees of freedom of biacetyl are frozen, the situation resembles the case of energy transfer from an atom to a diatomic molecule. A broad distribution of vibrational states may result [16, 17] (for experimental results see, for example, ref. 17).

Experimentally we find that quenching of biacetyl phosphorescence is accompanied by the appearance of a new broad red-shifted emission. The assignment of this emission to the B—X system is supported by a kinetic analysis. This assignment implies a very broad vibrational energy distribution, meaning that in this case electronic energy transfer is not a statistical process. The introduction of a single constraint and the use of an approximate information theory approach lead to a reasonable reproduction of the experimental results.

2. Experimental

Samples were handled in a greaseless vacuum line equipped with a capacitance manometer. Biacetyl (BDH Laboratories) and iodine (Baker analysed, 99.9% stated purity) were freshly distilled prior to use. The iodine pressure was usually controlled by putting a suitable slush bath around a cold finger attached to the fluorescence cell. Alternatively, the iodine pressure was measured directly in the cell. Ample time was allowed in this case for equilibration with wall absorption. In a clean well-pumped vacuum line this equilibration took several hours. The cell was made of a Pyrex tube 38 mm in diameter and 20 cm in length. Fluorescence was excited by a nitrogen-laser-pumped dye laser (Molectron DL 200 pumped by a Molectron UV-400 nitrogen laser). The laser output consisted of 5 ns pulses with an energy of about 200 μJ at a bandwidth of 1 cm^{-1}. Emission was collected at right angles and was focused onto the entrance slit of a $\frac{1}{4}$ m monochromator (Jarrel Ash). The spectral resolution in emission was varied between 3 and 6 nm. The light intensity was measured using a red-sensitive photomultiplier tube (Hamamatsu R928) connected to one of the following instruments: an oscilloscope or a box car integrator (PAR 162/164) for time-resolved studies, or a home-made gated electrometer [18] for time-integrated measurements. The electrometer gate could be opened either before or after the laser fired, with an OPEN interval of 2 - 80 μs. It could thus be used to reject scattered light and biacetyl fluorescence which were practically synchronous with the laser pulse and to retain the phosphorescence signal. The cell dimensions are too small for quantitative low pressure studies on long-lived emissions
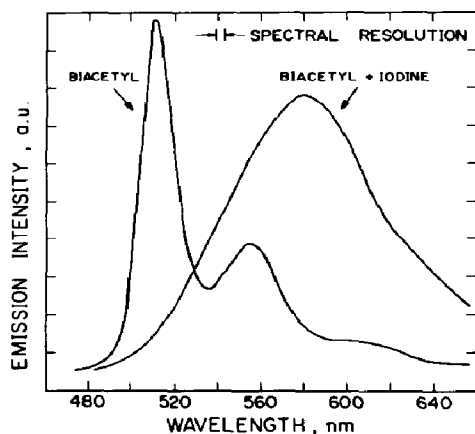
Fig. 2. Emission spectra of pure biacetyl and a biacetyl–iodine mixture, both excited at 435 nm. The biacetyl and iodine pressures were 0.2 Torr and 0.033 Torr respectively. The spectra are not drawn to the same scale.
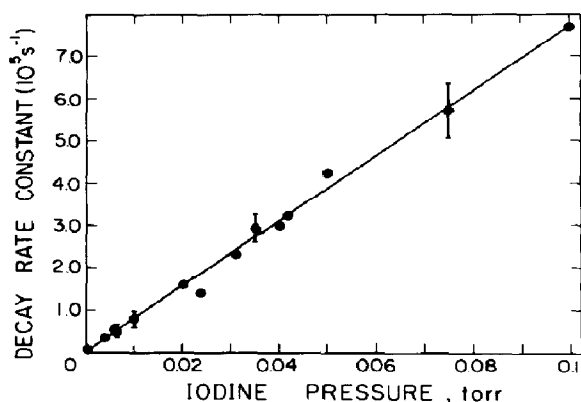
Fig. 3. The decay rate of biacetyl emission at 515 nm as a function of iodine pressure: biacetyl pressure, 1 Torr; k_q = (7.7 ± 0.5) × 10^6 $Torr^{-1}$ s^{-1}.

[19]. In the experiments reported here the emission decay time was usually shorter than 50 μs because of quenching by iodine. No corrections for diffusion and/or wall deactivation were necessary.

3. Results

3.1. Quenching of biacetyl phosphorescence by iodine

Irradiation of biacetyl at 435 nm resulted in the observation of the characteristic bright-green phosphorescence. Addition of even a minute amount of iodine led to a drastic reduction in the intensity of this emission and to the appearance of a weak deep-red emission. The spectra are reproduced in Fig. 2. The pressure of iodine used to obtain the spectrum shown in Fig. 2 was such that the characteristic 515 nm peak of biacetyl phosphorescence was too weak to be observed. At lower iodine pressures the spectrum consisted of a superposition of the two spectra shown.

The 1/e decay lifetime of the emission at 515 nm dropped from about 1.7 ms in the absence of iodine to 50 μs or less when iodine was added. This was taken as proof that the decay rate was determined by energy transfer to iodine. The dependence of this decay rate, measured at 515 nm, on iodine pressure is shown in Fig. 3. A distinct peak could be observed at 515 nm only as long as the iodine pressure was kept below 0.02 Torr. At higher pressures a smooth emission curve (cf. Fig. 2) was obtained with no discernible maximum at 515 nm. Notwithstanding, a Stern–Volmer representation yielded a straight line up to 0.1 Torr I_2 (Fig. 3). The quenching rate constant derived from the data, (7.7 ± 0.5) × 10^6 $Torr^{-1}$ s^{-1}, is practically equal to the gas kinetic rate constant, 8 × 10^6 $Torr^{-1}$ s^{-1}.
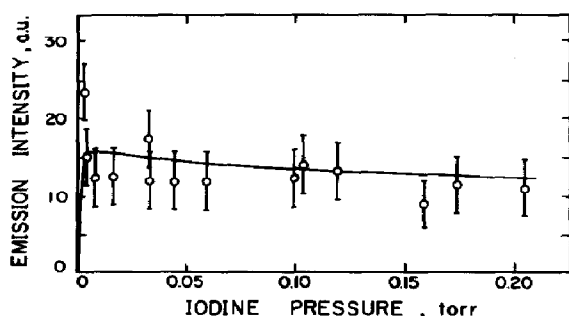
Fig. 4. Emission intensity (○) at 640 nm as a function of iodine pressure; ——, calculated using the model described in Section 4: biacetyl pressure, 1 Torr.
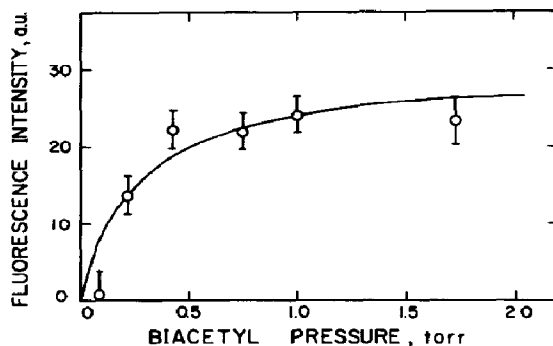
Fig. 5. Emission intensity (○) at 640 nm at a fixed iodine pressure (60 mTorr) as a function of biacetyl pressure; ——, calculated using the model described in Section 4.

3.2. Characterization of the red emission

The spectrum of the red emission was not changed, within experimental errors, by varying either the biacetyl or the iodine pressure, nor did it vary on scanning the excitation wavelength between 415 and 440 nm. The decay time of the red emission, as monitored at 575 or 640 nm, closely followed that of biacetyl, measured at 515 nm, at all iodine pressures. The intensity increased sharply with iodine pressure at low iodine densities. Increasing the pressure further led to a levelling-off of the intensity and possibly even to a slight decrease. The results for a biacetyl pressure of 1 Torr are displayed in Fig. 4. The quantity shown is the time-integrated intensity at 640 nm taking into account the changes in the emission lifetime. The large error bars are a result of some inherent difficulties encountered in these experiments. The red emission was relatively weak and at high iodine pressures interference from scattered laser light became a severe problem. It was eliminated by setting the delay time of the gated electrometer to 0.5 μs and as a result some of the red emission was also blocked. At low iodine pressures the contribution of biacetyl emission had to be subtracted from the observed intensity. Application of the appropriate corrections led to relatively large accumulative errors. Nevertheless, the steep initial rise and the essentially constant intensity at iodine pressures higher than 0.01 Torr are clearly shown in Fig. 4. The curve shown in Fig. 4 is a theoretical fit according to the model described in Section 4.

The effect of biacetyl pressure on the red emission intensity is shown in Fig. 5. The lifetime of the emission is practically constant. Thus, the time-integrated intensity is proportional to the signal amplitude in this case. As in Fig. 4 the signal increases with added gas pressure, albeit much more gradually. Again, an essentially constant value is reached at a relatively low pressure (approximately 1 Torr).
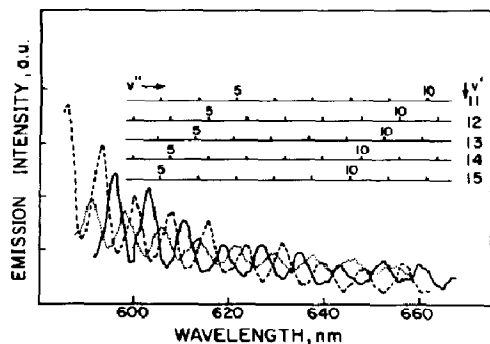
Fig. 6. Emission spectra of iodine following excitation at various wavelenths: - - -, λ_{exc} = 578 nm; $\cdots$, λ_{exc} = 583 nm; ——, λ_{exc} = 588 nm. A partial vibrational assignment, based on the spectroscopic constants of ref. 20, is also shown.

TABLE 1

Quenching rate constants of iodine B–X emission by biacetyl

λ_{exc} (nm)	v'	k ($\times\ 10^6$ Torr^{-1} s^{-1})
567.7	17	16 ± 3
556.2	21	12 ± 2
546.1	25	13 ± 3
511.3	46	8.3 ± 1.6
501.0	63	8.0 ± 1.5

3.3. Quenching of iodine emission by biacetyl

Direct excitation of iodine to a given v' level of the B state results in a characteristic well-defined emission spectrum. It consists of a sequence of bands that may be assigned to progressions due to the initially excited state, or states, differing by one vibrational quantum. The addition of biacetyl does not appreciably change the spectral distribution. Spectra following excitation at slightly different energies are clearly distinguishable in Fig. 6. At room temperature the linewidth of the laser is not narrow enough to excite a single v' state. Thus, irradiation at 578 nm populates the v' = 14, 16 and 18 levels and irradiation at 588 nm populates the v' = 11, 13 and 15 levels. The emission spectrum contains several progressions, the components of which appear as fairly broad bands in the spectrum (Fig. 6). An added pressure of biacetyl, as in the case of many other collision partners (*e.g.* methyl iodide, trifluoroiodomethane and cyanogen iodide), does not affect the shape of the spectrum but strongly decreases the intensity. As in the reverse process, quenching rate constants are extremely large, sometimes exceeding gas kinetic values. The results for some v' levels are listed in Table 1.

3.4. A search for ground state interaction between biacetyl and iodine excimer formation and a permanent chemical change following irradiation

The appearance of the red emission might conceivably be a result of complex formation. In an attempt to check this possibility we recorded the visible absorption spectra of iodine–biacetyl mixtures at various pressures up to 0.25 Torr I_2 and 40 Torr biacetyl. The spectra obtained were identical with those of the individual components in all cases within the precision of the experiment. Thus, no ground state complex formation is indicated.
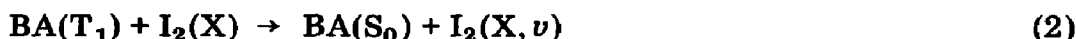
Another species that might produce the red emission is an excimer, or a long-lived collision complex between excited biacetyl and ground state iodine. The lifetime of such an excimer, as well as its emission intensity, is expected to be a function of the iodine/biacetyl pressure ratio. The emission lifetime was carefully measured for a large number of mixtures in which the iodine pressure was varied between 0.003 and 0.3 Torr and the biacetyl pressure was varied between 0.2 and 10 Torr. The decay kinetics, as measured at 630 nm, always followed the rate predicted by the rate constant quoted in Section 3.1. This indicates that the lifetime of an excimer, if present in the system, is much shorter than that of triplet biacetyl for all the pressures employed. This result suggests that a long-lived complex is not formed or that the decay kinetics are governed by the decay of the parent biacetyl.

Finally, the interaction between triplet biacetyl and iodine might lead to a permanent chemical transformation initiated, for example, by iodine atoms. We tried to observe a change in the iodine concentration following irradiation of a mixture at 435 nm for 3 h, monitoring the iodine concentration using direct absorption and using fluorescence excitation (at 576 nm). During this period more than 10 photons were deposited in the sample on the average for each iodine molecule. At the same time the iodine concentration remained constant within the experimental error (±5%).

4. Discussion

4.1. Possible mechanisms for biacetyl phosphorescence quenching by iodine

The rate constant for biacetyl quenching measured in this work is very large — probably the highest reported to date for this molecule. Several possible channels in addition to process (1) can be proposed to account for this high efficiency, *e.g.*

$$BA(T_1) + I_2(X) \rightarrow BA(S_0) + I_2(X, v) \qquad (2)$$

$$\rightarrow BA \cdot I_2 \text{ complex} \qquad (3)$$

$$\rightarrow BA(S_0) + 2I \qquad (4)$$

Using luminescence data only, as in this work, it is not possible to provide a unique assignment.

The appearance of the red emission provides a clue — part of the energy is evidently channelled to another electronically excited species. To assess

the quantitative importance of this channel the fluorescence quantum yield must be known. As detailed in Section 4.2 the most likely emitting species is iodine in the B state, formed by direct energy transfer. This assignment, coupled with measurements of the total light yield associated with the red emission, leads to an estimated contribution of $(8 \pm 3)\%$ by this channel. In this section we provide circumstantial evidence that process (4), dissociative energy transfer to form two iodine atoms, is the major quenching process. Our arguments are mainly based on analogy with other quenching gases and on the elimination of other possibilities.

Process (2), in which the electronic state of iodine does not change, is essentially a collision-induced [21] $T_1 \rightarrow S_0$ intersystem crossing in biacetyl with iodine serving as the collision partner. The efficiency of this process is strongly dependent on the spin–orbit coupling constant. This coupling can be greatly enhanced by collisions with a heavy atom, making process (2) quite plausible. The element following iodine in the periodic table (xenon) is, however, a very poor quencher of triplets [22]. Literature data, reconfirmed by direct measurement, led to a rate constant which was 5 orders of magnitude smaller than that of iodine. Similarly, organic iodides [6] are very poor quenchers as well. It is concluded that process (2) can be neglected for all practical purposes.

No positive evidence pointing to the formation of a stable complex in process (3) could be obtained. It may, of course, exist as a short-lived intermediate in process (1) or process (2) — a proposition not ruled out by our results.

Process (4) is energetically allowed as $E(T_1)$ is higher than the dissociation energy of iodine (12 440 cm^{-1}, Fig. 1) and also slightly higher than dissociation to I + I*, where I* denotes I($5^2P_{1/2}$). A comparison with molecular oxygen is instructive. Oxygen is a fairly potent quencher of the biacetyl triplet (Section 1) but is still about 300 times weaker than iodine. In both cases spin conservation is not a limitation but the dissociation energy of oxygen (approximately 40 970 cm^{-1}) [12] is much higher than $E(T_1)$.

Several routes [12, 23] can lead to the dissociation of iodine: direct transfer to a repulsive state (e.g. $^3\Sigma_{0u^-}$ or $^3\Pi_{0g^+}$), population of a predissociative state (the B state or the shallow $A^3\Pi_{1u}$ state) or population of a repulsive state belonging to the ground electronic state. In each case iodine atoms may, in principle, be observed using a chemical scavenger. In the absence of a suitable scavenger the most likely process is atom–atom recombination [24]. In that case iodine atoms might be monitored in direct absorption measurements. Appropriate experiments are now planned.
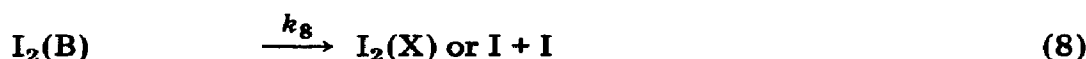
4.2. Assignment of the red emission to the B–X fluorescence system: a kinetic model

In the absence of evidence pointing to a biacetyl–iodine complex or to an excimer (Section 3.4) a probable candidate for the origin of the red emission is the iodine B state. It may be formed by several pathways, *e.g.* by recombination of iodine atoms (reverse predissociation). Although the

existence of iodine atoms in the system, and consequently recombination, is proposed in Section 4.1, the process is not likely to lead to the emission observed. This conclusion follows mainly from the short rise time of the emission (up to about 50 ns). Although three-body rate constants with biacetyl are not known, reported values for other collision partners [24] lead to rise times that are many orders of magnitude longer.

Direct population of the B state by energy transfer, process (1), can be shown to account adequately for the time-resolved evolution as well as for the effect of iodine and biacetyl pressures on the emission intensity. Kinetic modelling is complicated by the fact that a broad distribution of vibrational states is involved (see Section 4.3). Equations such as eqn. (1) have to be written for every vibrational level v' of the B state as well as for the processes (5) - (8):

$$I_2(B) + BA(S_0) \xrightarrow{k_5} I_2(X) + BA(S_0) \tag{5}$$

$$I_2(B) + I_2(X) \xrightarrow{k_6} 2I_2(X) \tag{6}$$

$$I_2(B) \xrightarrow{k_7} I_2(X) + h\nu \tag{7}$$

$$I_2(B) \xrightarrow{k_8} I_2(X) \text{ or } I + I \tag{8}$$

A complete model would require the use of many rate constants, some of which are known or can be independently obtained (e.g. k_5, k_6 and k_7) and some that are unknown (e.g. k_1). In the present treatment we assume that the rate constants are independent of v'. The variation of k_5 - k_8 with v' is not very large (Table 1 and ref. 25). Population rates of different v' states by energy transfer are likely to span a larger range. In fact preferential population of some states is required to account for the spectrum observed. However, states that are formed with a small rate constant are not likely to contribute significantly to the emission spectrum. In Section 4.3 we show that even if a broad distribution is involved it is probably limited to 10 - 20 vibrational states, spanning an energy range of about 1500 cm^{-1}. For the contributing states we use an average rate constant that is equal to the quenching rate constant observed divided by an appropriate factor (see later).

The time evolution of the B state may now be written

$$\frac{d[I_2^*]}{dt} = k_1[BA^*][I_2] - k_5[I_2^*][BA] - k_6[I_2^*][I_2] - (k_7 + k_8)[I_2^*] \tag{9}$$

Here $[I_2^*]$ and $[BA^*]$ denote the concentrations of B state iodine molecules and triplet biacetyl molecules respectively; k_7 and k_8 are the collision-free radiative and non-radiative decay rate constants respectively. Triplet biacetyl is assumed to be formed instantaneously by the laser pulse and to decay exponentially according to
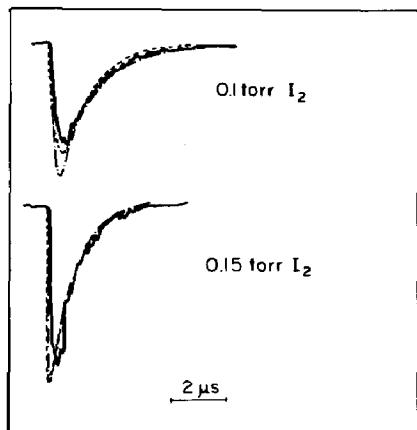
Fig. 7. Experimental (——) and calculated (- - -, $k_1 = k_q/10$; —·—·, $k_1 = k_q/30$) decay curves: biacetyl pressure, 0.87 Torr; $\lambda_{em} = 585$ nm. The rate constants used in the calculation are discussed in the text.

$$[BA^*] = [BA^*]_0 \exp\{-(k_q[I_2^*] + k_d)t\}$$

where k_q is the total quenching rate constant of biacetyl by iodine derived from all channels and k_d is the collision-free decay time involving both radiative decay and intersystem crossing to S_0. The rate constants used in the calculation were $k_q = 7.7 \times 10^6$ Torr^{-1} s^{-1}, $k_1 = k_q/10$ or $k_1 = k_q/30$, $k_5 = 7 \times 10^6$ Torr^{-1} s^{-1}, $k_6 = 1.4 \times 10^7$ Torr^{-1} s^{-1} and $k_7 + k_8 = 3 \times 10^5$ s^{-1}. The build-up and decay of the emission signal observed at 585 nm are compared with the calculation in Fig. 7. An upper limit to k_1 is $k_q/10$, as the population of the B state accounts for about 10% of the total quenching (Section 4.1). If emission from a single v' state were monitored, a much smaller value would have to be used. In view of the low resolution of the emission spectrum and the fact that many states contribute to the emission at about 585 nm, we estimate that at least one-third of the vibrational states contribute to the signal. Thus $k_q/30$ is a reasonable lower limit for k_1. As is shown in Fig. 7, varying k_1 between $k_q/10$ and $k_q/30$ makes a rather small difference in the computed signal. In contrast, changing k_q or the other rate constants by a factor of 5 or more led to serious disagreement with the experimental data.

The same rate constants were used to calculate the effect of changing the iodine or the biacetyl pressure on the signal intensity. As is shown in Figs. 4 and 5, the experimental dependence is reasonably well reproduced. This fit to three independent experiments suggests that the assignment of the red emission to the B–X system is a plausible postulate.

Agreement with a proposed mechanism never constitutes a *proof* of its validity. The present case is no exception to that rule and the simplifying assumptions, though reducing the number of adjustable parameters, actually prevent the construction of a faithful model. The main result of the analysis is thus the claim that B state emission is not ruled out on kinetic grounds.

4.3. The vibrational distribution leading to the spectrum observed

Irradiation of iodine, even in the presence of biacetyl, using a narrow-band laser leads to a vibrationally well-resolved spectrum (Fig. 6). Simultaneous excitation of a few (2 or 3) vibrational levels of the B state still maintains the same overall appearance. This must be because electronic decay (radiative or non-radiative) is faster than extensive vibrational relaxation. If the reverse situation were to hold, the emission spectrum observed would be either very broad (because there are many participating states) or red shifted and independent of the excitation wavelength (if complete relaxation to $v' = 0, 1$ took place).

Inspection of Fig. 6 suggests that simultaneous population of *many* v' levels can lead, under the spectral resolution employed, to a broad seemingly structureless spectrum. Assignment of the red emission to the B–X system therefore involves a broad distribution of vibrational states. In this section we use the formulation of information theory [26] to show that a single constraint imposed on the system can lead to a fairly broad distribution. Available Franck–Condon factors are then used to show that a broad spectrum is generated.

The excess energy that has to be distributed among the translational, rotational and vibrational degrees of freedom of biacetyl and iodine following process (1) is about 4600 cm^{-1}. The situation is formally similar to the case of an elimination of a diatomic fragment from a large molecule [27]. In many reactions of this type considerable vibrational excitation of the diatomic molecule, *e.g.* HF, was observed. The vibrational state distribution could often be characterized as having a linear surprisal:

$$P(v) = P°(v) \exp(- \lambda_v f_v - \lambda_0) \tag{10}$$

where $P(v)$ is the fraction of events leading to a diatomic in the state v, $P°(v)$ is the prior distribution [28] and $f_v = E_v/E$ where E_v is the energy of the v state and E is the total available energy. A large negative value of λ_v indicates extensive vibrational excitation. The prior distribution can be calculated from the known vibrational and rotational levels of biacetyl and iodine. In view of the considerable computational effort involved, several simple analytical approximations have been shown to provide a faithful description of the system. One approximation which is frequently used is the rigid rotor harmonic oscillator approximation, which in this case leads [28] to

$$P°(v) = (s + 4)^{-1}(1 - f_v)^{s+3} \tag{11}$$

where s is the number of vibrational modes of biacetyl. Combining eqn. (10) with eqn. (11) leads to the expected distribution

$$P(v) = (s + 4)^{-1}(1 - f_v)^{s+3} \exp(- \lambda_v f_v - \lambda_0) \tag{12}$$

Of the 30 vibrational modes of biacetyl [14], six are C—H stretching modes with $E_v \approx 3000$ cm^{-1}. These modes are not expected to be appreciably populated in view of the small total available energy. Consequently,
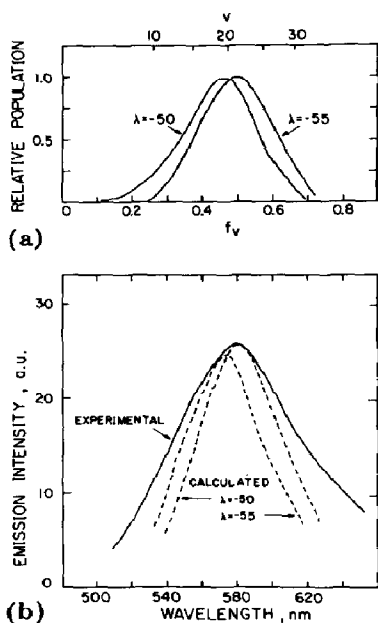
Fig. 8. (a) The vibrational distributions of $I_2(B)$ calculated using eqn. (11). (b) Experimental (——) and computed (- - -) spectra of a biacetyl–iodine mixture. The vibrational distributions shown in Fig. 8(a) were used in the calculations.

s was set to be 24. E_v for iodine was calculated using ω_e and $\omega_e x_e$ from ref. 20. The harmonic oscillator approximation leads to a large error in f_v at the high ($v > 20$) values required to reproduce the spectra. The distributions that appear to reproduce the spectrum most accurately involve rather large λ_v values, as shown in Fig. 8(a).

Reconstruction of the resulting spectrum requires knowledge of the emission spectra due to each vibrational level. In principle, spectra such as those displayed in Fig. 6 may be used for this purpose. In practice a careful analysis is required, as they often involve excitation of more than one level (see ref. 25). The separation into individual bands can introduce a fairly large error, and it appeared to be safer to use the recent tabulation of Franck–Condon factors given by Tellinghuisen [29]. Unfortunately, these are available only for $v'' = 0 - 5$. (We used the Franck–Condon factors given in ref. 29. Values for some selected levels up to $v'' = 9$ are listed in a more recent work [30] where deviations from previous calculations are reported but are not discussed.) Furthermore, an intensity profile for each band had to be assumed. We used a triangular form with a maximum intensity (at the frequency calculated for the band origin) set in proportion to the Franck–Condon factor and with zero intensity at the midpoint between neighbouring bands. (This shape was suggested from Fig. 6.)

The resulting spectrum (Fig. 8(b)) is quite smooth and exhibits a maximum at about 580 nm for $\lambda_v = - 50$. The spectral width is seen to be significantly smaller than the experimental width. This may be partly because only $v'' = 0 - 5$ states were used. Obviously, higher v'' states contribute but

could not be included consistently into the analysis since the necessary Franck–Condon factors are not available [29]. A further possible source of error may be the use of too many vibrational modes of biacetyl. For instance, the two C=O stretching vibrations at 1700 cm^{-1} are expected to contribute little. A smaller s value would lead to a broader distribution. In the absence of better spectroscopic input a complete match with the observed spectrum might be fortuitous. It is felt that the calculated spectrum bears sufficient resemblance to the experimental spectrum to provide further support to the proposed assignment.

If we accept the assignment of the red emission to the B–X fluorescence we may estimate the efficiency of process (1). The total (time- and wavelength-integrated) emission intensities of pure biacetyl and of the red emission were measured using the same optical geometry. Using an average value (over the relevant v' states) for the quantum yield of fluorescence from iodine it was established that, when the phosphorescence of biacetyl is completely quenched, the red emission accounts for only $(8 \pm 3)\%$ of the missing photons. This result was quoted as supporting the involvement of dissociative energy transfer (*cf.* Section 4.2) and was used in the kinetic model (by setting k_1 equal to $k_q/10$ or $k_q/30$).

5. Conclusions

Electron energy transfer from biacetyl to iodine is extremely efficient. Energy considerations and analogy with other quenchers point to dissociative energy transfer as a major route but positive confirmation is awaited from the direct monitoring of iodine atoms. This conclusion is indirectly supported by the assignment of the red emission appearing in the mixture to the B–X fluorescence system of iodine. The broad structureless emission may result from a non-statistical distribution of vibrational levels of iodine in the B state. A crude single-parameter fit using information theory is seen to reproduce the data fairly well. This model implies high vibrational excitation (actually a population inversion).

Acknowledgments

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