matrix element for an atomic transition is

$$\langle{}^{2s'+1}l_{J_b'}J_b' \,\|\, \sum_j er_{j_b}{}^{l_b}T_{l_b}(\hat{r}_j) \,\|\, {}^{2s+1}l_{J_b}J_b\rangle = (2J_b+1/2J_b'+1)^{1/2}C(J_bl_bJ_b';000)$$

$$\times\langle \mathbf{R}({}^{2s'+1}l_{J_b'}) \,\|\, \sum_j er_{jb}{}^{l_b} \,\|\, \mathbf{R}({}^{2s+1}l_{J_b})\rangle = (2J_b+1/2J_b'+1)^{1/2}C(J_bl_bJ_b';000) \int \mathbf{R}({}^{2s'+1}l_{J_b'})er_b{}^{l_b}\mathbf{R}({}^{2s+1}l_{J_b})r_b{}^2dr_b, \quad (4)$$

where $\mathbf{R}({}^{2s+1}l_{J_b})$, equal to $R(nl)/r$ in the hydrogenic atom,[2] is the radial wavefunction of the atom. This reduced matrix element is related to the lifetime (τ) and Einstein's coefficient (A) for spontaneous (multipole) emission of the atomic state as:

$$\tau^{-1} = A_{J_b\rightarrow J_b'}(2^{l_b}-\text{pole}) = 4\pi(l_b+1)(2\pi\nu)^{2l_b+1}S_{l'\leftarrow l}(J_b\rightarrow J_b')/hl_b(2l_b+1)[(2l_b-1)!!]^2c^{2l_b+1}(2J_b+1)$$

$$= [4\pi(l_b+1)(2\pi\nu)^{2l_b+1}(2J_b'+1)/hl_b(2l_b+1)[(2l_b-1)!!]^2c^{2l_b+1}(2J_b+1)] \,|\, \langle{}^{2s'+1}l_{J_b'}J_b' \,\|\, er^lT_l \,\|\, {}^{2s+1}l_{J_b}J_b\rangle \,|^2. \quad (5)$$

The corresponding matrix elements for the diatomic molecule have been given in Paper I.

For dipole–dipole interaction $l_a = l_b = 1$, the total cross section is

$$\sigma = \tfrac{2}{3}(2\mu/\hbar^2)^2k^{-2} \sum_{\text{doubling}} \sum_L \sum_{L'} \pi^3(2L+1)(2J_a+1)^{-1}(2J_b+1)^{-1}S_{\lambda\leftarrow\Lambda}(J_a\rightarrow J_a')S_{l'\leftarrow l}(J_b\rightarrow J_b')C^2(L,2,L';000)$$

$$\times [S_{n'n}{}^{\lambda\Lambda}]^2\left[\int_0^\infty J_{L'+1/2}(k'R)J_{L+1/2}(kR)/R^2dR\right]^2. \quad (6)$$

For the $6\,{}^1S_0 - 6\,{}^3P_1$ transition of the mercury atom, if we take the lifetime[3] $\tau = 1.08\times10^{-7}$ sec, then from Eq. (5):

$$1/\tau = A_{0\rightarrow1}(2-\text{pole}) = (64\pi^4\nu^3/3c^3h)S({}^1S_0\rightarrow{}^3P_1)$$

$$= (64\pi^4\nu^3/3c^3h)C^2(011,000)\langle \mathbf{R}({}^3P_1) \,|\, er \,|\, \mathbf{R}({}^1S_0)\rangle^2$$

$$= (64\pi^4\nu^3/3c^3h)M^2({}^1S_0 - {}^3P_1). \quad (7)$$

The transition moment $M({}^1S_0 - {}^3P_1)$ may be estimated to be 0.694 D. Similarly, the line strength and transition moment[1] etc., for the diatomic molecule can be obtained from experimental lifetime or oscillator strengths.

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Comments

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Comments on Molecular Nonradiative Transition Probabilities in the Statistical Limit

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Nonradiative molecular decay in the statistical limit[1–6] can be considered as multiphonon process,[7–10] the thermally averaged transition probability $\langle W\rangle$ being expressed as a weighted density of states function[9–11]

$$\langle W\rangle = \sum_i p(si)W_{si},$$

where

$$W_{si} = \sum_j |V_{si,lj}|^2\,\delta(E_{si} - E_{lj})$$

is represented by a Fourier transform of a generating function which can be recast in terms of Green's functions for nuclear motion[7–10] while W_{si} can be expressed applying Feynman's operator techniques[12,13]

$$\langle W\rangle=\hbar^{-2}\int_{-\infty}^{\infty} f(t)\, \exp(-i\Delta Et/\hbar)\,dt,$$

where $f(t)=Z^{-1}\,\mathrm{Tr}(V_{sl}G_lV_{ls}G_s)$. Siebrand argued[14] that a specific result of this scheme[9,10] is just a special limiting case of his formulas.[15–18] Although Siebrand's treatment is valid in the weak coupling limit, it should be noted that the multiphonon formalism[9,10] is more general and can be expressed in a useful form whenever the nuclear motion in the two electronic states can be factored into independent vibrational modes, which are not necessarily harmonic or characterized by the same frequency. For the simplest model system involving displaced potential surfaces[9,10] $\langle W\rangle$ is given by Eq. (IV 6) of Ref. 10. When frequency changes are included, a more complex result was obtained [Ref. 10, Eqs. (III 4) and (A-1)–(A-6)]. This general scheme[9,10] does not involve any auxiliary assumptions concerning the grouping of molecular frequencies.[14–18,19] We would like to emphasize that the weak coupling limit[9,10] [Eq. (IV 6), Ref. 10], which can be handled numerically[13] or by the saddle point integration method,[9] just provides a special case of the general formalism. $\langle W\rangle$ is then dominated by the highest vibrational frequencies,[9,10] however, the contributions of the lower frequencies can be systematically incorporated.[10]

The main accomplishments of the general treatment are:

(a) General formulas for W_{si} and for $\langle W\rangle$ are provided,[9,10,13] amenable to numerical calculations,[13] and analytic approximations.[9,10]

(b) The strong coupling limit,[9,10] corresponding to the Teller model,[20] reduces at high temperatures to an activated rate equation.[9,10]

(c) The nature of propensity rules and the effective energy gap in the weak coupling situation were elucidated.[10]

(d) Low frequency vibrations of an inert medium do not contribute to $\langle W\rangle$ in the statistical limit.[10]

(e) Explicit expressions for $\langle W\rangle$ and for W_{si} were derived only for harmonic potentials for which the Green's functions are known.[9,10] Anharmonicity corrections[16–18] are important from the quantitative point of view, and a similar controversey prevailed in the classical theory of unimolecular reactions.[21] No one believes in harmonic molecules in real life, however, they provide useful models for a wide class of radiationless processes.

(f) Nonharmonic modes can be handled by displaying the Fourier integral in terms of a convolution, factoring out modes corresponding to strongly anharmonic vibrations for electronic relaxation,[10] twisting modes for *cis–trans* isomerization[22] or repulsive states in the quantum theory of unimolecular decomposition.[23]

(g) A general expression for the decay probability W_{si} of a single vibronic level can be handled by Feynman's operator techniques[12,13] yielding theoretical results for optical selection studies.[13]

(h) A version of this method was utilized for the study of the coupling between electronic and vibrational relaxation.[24]

(i) This scheme was applied for unimolecular thermal decomposition reactions.[23]

These examples serve to demonstrate the wide implications and applications of the multiphonon formalism, for a wide class of radiationless processes, which we believe to be much more general than the approximate evaluations of Franck Condon factors[14–18] for electronic relaxation.

Finally, consider the validity conditions for the statistical limit[1,3–6] discussed by Siebrand.[14] The requirement of constant ϵ and constant V in the Bixon–Jortner model[1] involves a grossly oversimplified model which, although not encountered in real life, is very useful for establishing physical criteria for the irreversibility of the nonradiative decay in isolated large molecules[1,3–6] and for distinguishing between the implications of interstate coupling and intramolecular relaxation.[1,25] A similar pedagogic approach was adopted in nuclear physics.[26] Obviously, the delta functions in W_{si} are used for bookkeeping purposes,[10] and the general expression resulting from the theory of consecutive decay[4,5] is

$$W=\sum_i p(si)W_{si}(E_{si}),$$

where

$$W_{si}(E)=\sum_j \Gamma_{lj}\,|V_{si,lj}|^2\bigg/\left[(E-\tilde{E}_{si})^2+\left(\frac{\Gamma_{lj}}{2}\right)^2\right].$$

Γ_{lj} is the width of the final zero order state resulting from externally induced vibrational relaxation,[4] radiative decay in internal conversion[4] or infrared emission.[1] The statistical limit[1,3,6] is encountered when the line shape function $W_{si}(E)$ is a smoothly varying function of the energy[4,5] in the vicinity of $E\simeq E_{si}$, which implies that [4,5] $\langle\epsilon\rangle\ll\Gamma_{lj}+\hbar/t_m$, where t_m is the upper time limit for experiment[1,3,5] and $\langle\epsilon\rangle$ the mean level spacing. In the statistical limit[4,23] W_{si} and $\langle W\rangle$ are independent of Γ_{si}. In the case $\langle\Gamma_{lj}\rangle=0$, the Bixon model is regained, while medium perturbation (contributing to $\langle\Gamma_{lj}\rangle$) will make some excited electronic states, corresponding to the intermediate case in the isolated molecule[4,25] to exhibit statistical behavior when the molecule is imbedded in an inert medium.[4,27]

These comments were inspired by two recent notes by Siebrand[14] and Fischer.[28]

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Comment on the Spin–Orbit Contribution to the Zero-Field Splitting of the Oxygen Molecule

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Recently, Zamani-Khamiri and Hameka[1] (ZKH) calculated the spin–orbit contribution to the O_2 zero-field splitting $D=2\lambda_{ss}+2\lambda_{so}$ to be $\lambda_{so}=0.156$ cm^{-1}. Pritchard, Bender, and Kern[2] have performed *ab initio* studies on the spin–spin effects. They find that $\lambda_{ss}=0.756$ cm^{-1} in the near Hartree–Fock limit and that configurational mixing decreases λ_{ss} in the minimal-basis-set approximation.[3] Inasmuch as the experimental value of $\lambda=\lambda_{ss}+\lambda_{so}=1.98$ cm^{-1} given by Tinkham and Strandberg[4] is in significant disagreement with the sum of these respective computed values, we decided to repeat the ZKH work using the spin–orbit option of recently developed fine-structure programs.[5] We obtain $\lambda_{so}=0.628$ cm^{-1} which is about 4 times larger than that reported by ZKH.

Detailed examination of the calculation shows that the main point of departure with ZKH is in the values of the atomic integrals listed in Tables II–IV of Ref. 1. The revised values are given in Table I of this Note. They are accurate to the last figure quoted. The most important differences involve the one-center, spin-other-orbit integral w_{73} from Group II, the Coulomb integrals w_{71} and w_{76} from Group III, and those hybrid integrals from Group IV footnoted "c". As a result, the contributions $w_{II}-w_{IV}$ must be revised as follows: $w_{II}=56.52i$, $w_{III}=2.73i$, $w_{IV}=-2.92i$, all in cm^{-1}. The individual exchange integrals (Group V) were not compared; however, their collective effect now amounts to only $w_V=-0.088i$ cm^{-1}. Combination of the one-electron spin–orbit term $w_I=$