in the form

$$\int_{-1}^{1} \exp(iy\mu \, \cos\psi) J_m[y(1-\mu^2)^{1/2} \, \sin\psi] P_{k+m}{}^m(\mu)d\mu$$
$$= 2i^k P_{k+m}{}^m(\cos\psi) j_{k+m}(y), \quad (A4)$$

where $j_n(x)$ is a spherical Bessel function defined by

$$j_n(x) = (\pi/2x)^{1/2} J_{n+1/2}(x). \quad (A5)$$

Let

$$y = (KR/2)(\lambda^2 - \sin^2\delta)^{1/2} \quad (A6)$$

$$\cos\psi = \lambda \, \cos\delta/(\lambda^2 - \sin^2\delta)^{1/2}; \quad (A7)$$

then

$$\sin\psi = (\lambda^2 - 1)^{1/2} \sin\delta/[\lambda^2 - \sin^2\delta]^{1/2}. \quad (A8)$$

Substituting Eqs. (A6)–(A8) into Eq. (A4), we find an integral of the same form that appears in Eq. (A3),

and it follows that

$$I_k{}^m = 4\pi i^k \int_1^{\infty} f(\lambda) j_{k+m}(y) P_{k+m}{}^m(\cos\psi)d\lambda. \quad (A9)$$

Using these results, Eqs. (12)–(14) are easily verified.

Assuming that Eq. (A9) cannot be evaluated analytically, the following numerical scheme was used for this purpose. A program for a digital computer, the Control Data Corporation's 1604, was written which carried out the integration of Eq. (A9) for a given choice of K, δ, R by means of Weddle's quadrature formula. With these values it is then possible to evaluate Eq. (12). The sum in Eq. (12) was usually truncated to three terms, although four terms were used in some cases. The same program was used to evaluate $\epsilon(K,\delta,R)$ and carry out the integration of Eq. (6).

ΔS = ±1 Magnetic Multipole Radiative Transitions*

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The magnetic multipole transition probability is calculated in terms of the matrix elements of the magnetic multipole. The magnetic jm moment $Q_{jm}{}^{(mg)}$ is defined as

$$(e/\mu)[4\pi/(2j+1)]^{1/2} \sum_i (\boldsymbol{\nabla} r_i{}^j Y_{jm})[(j+1)^{-1} \mathbf{l}_i + \mathbf{s}_i],$$

where e and μ are electron charge and electron mass, r_i, $\mathbf{l}_i$, and $\mathbf{s}_i$ are the coordinate, orbital angular momentum, and spin-angular momentum of the ith electron and Y_{jm} is the spherical harmonic. Magnetic quadrupole and octupole moments are explicitly given. It is shown that for the $^3\Sigma_u{}^+ \leftrightarrow \,^1\Sigma_g{}^+$ transition of the hydrogen molecule, the magnetic quadrupole transition is more important than the conventional spin-orbit electric dipole transition. The magnetic octupole transition has the same order of magnitude as the spin-orbit magnetic dipole transition.

INTRODUCTION

THE transition between states with different multiplicity is a very weak one. The corresponding emission line of some ions were first found in the spectra of some nebulas[1] and the theory has been given by Condon and other people.[2] This type of transition has been investigated for many ions since then, a brief review can be found in Garstang's article.[3] In all these theories the mixing of different multiplicity states through the spin-orbit interaction was assumed to be important. The $^1D_2$ state of O III, for example, has

0.0074 of $^3P_2$ wave function mixed through the spin-orbit interaction, and the transition to a triplet state can occur through this small part of the wave function. Most of the phosphorescences of molecules are interpreted as due to the singlet-triplet transition.[4] McClure first suggested the transition through the spin-orbit interaction for these molecules.[5] The present author and Koide formed a theory starting with the Dirac equation of electron and calculated the singlet-triplet transition probability of the benzene molecule.[6] The result with some approximation gave about 1 sec for the lifetime of the lowest $^3B_{2u}$ state of this molecule. Hameka and Oosterhoff[7] refined the calculation and showed the lifetime of the same state to be 190 sec. Calculations for

* Supported by National Science Foundation.
[1] I. S. Bowen, Astrophys. J. 67, 1 (1928).
[2] See C. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), pp. 282–283.
[3] R. H. Garstang, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Part 1.

[4] M. Kascha, Chem. Rev. 41, 401 (1947).
[5] D. C. McClure, J. Chem. Phys. 17, 665 (1949).
[6] M. Mizushima and S. Koide, J. Chem. Phys. 20, 765 (1952).
[7] H. F. Hameka and L. J. Oosterhoff, Mol. Phys. 1, 358 (1958).

other molecules have also been done following the same idea, and they are briefly reviewed by Garstang.[3]

In this paper a completely different mechanism, namely, the magnetic multipole transition is proposed. If the probability of the electric dipole transition is $P_1{}^{(\text{el})}$, the conventional theory of $\Delta S=\pm1$ transitions gives the probability of about $(\hbar\omega/\mu c^2)^2P_1{}^{(\text{el})}$ for the case of spin-orbit electric dipole transition, since the spin-orbit coupling is a first-order relativistic correction to the Coulomb energy which is about $\hbar\omega$. $\hbar\omega$ is the photon energy which appears or disappears in our transition and μc^2 is the rest-mass energy of the electron. It will be shown that the magnetic quadrupole transition has the probability of the same order of magnitude, namely, $(\hbar\omega/\mu c^2)P_1{}^{(\text{el})}$. In the same way one can show that the spin-orbit magnetic dipole transition has the same order of magnitude as the magnetic octupole transition.

MAGNETIC MULTIPOLE TRANSITION PROBABILITY

The theory of the spherical photon is given in Akhiezer and Berestetsky's book.[8] They showed that the electric field for a photon which is the eigenstate of the total angular momentum with eigenvalues j and m, and the eigenstate of the energy with eigenvalue $\hbar\omega$ and at the same time the eigenstate of the parity operator with eigenvalue $(-1)^{j+1}$, is

$$\mathbf{E}_{\omega jm}=\boldsymbol{\mathcal{E}}_{\omega jm}+\boldsymbol{\mathcal{E}}_{\omega jm}{}^*,\tag{1}$$

$$\boldsymbol{\mathcal{E}}_{\omega jm}=(\hbar\omega^3/16\pi^3\epsilon_0c^2)^{1/2}e^{-i\omega t}g_j(\omega r/c)\mathbf{Y}_{jjm}(\mathbf{r}/r),\tag{2}$$

where ϵ_0 is the permittivity of the vacuum and

$$g_j(\omega r/c)=(2\pi)^{3/2}i^jJ_{j+1/2}(\omega r/c)/(\omega r/c)^{1/2},\tag{3}$$

with the Bessel function $J_{j+1/2}$, and $\mathbf{Y}_{jjm}(\mathbf{r}/r)$ is the spherical vector given by the spherical harmonics $Y_{jm}(\mathbf{r}/r)$ as

$$\mathbf{Y}_{jjm}(\mathbf{r}/r)=\begin{bmatrix}[(j+m)(j-m+1)]^{1/2}Y_{jm-1}+[(j-m)(j+m+1)]^{1/2}Y_{jm+1}\\i[(j+m)(j-m+1)]^{1/2}Y_{jm-1}-i[(j-m)(j+m+1)]^{1/2}Y_{jm+1}\\2mY_{jm}\end{bmatrix}[4j(j+1)]^{-1/2}.\tag{4}$$

There exists another state with the same ω, j, and m eigenvalues, but with the parity of $(-1)^j$. Such state is called an electric state while our state is called a magnetic state. In this paper we are interested in the magnetic states only.

If we take the Coulomb gauge we see from (2) that the vector potential $\mathbf{A}_{\omega jm}$ is

$$\mathbf{A}_{\omega jm}=\mathcal{A}_{\omega jm}+\mathcal{A}_{\omega jm}{}^*,\tag{5}$$

$$\mathcal{A}_{\omega jm}=i(\hbar\omega/16\pi^3\epsilon_0c^2)^{1/2}e^{-i\omega t}g_j(\omega r/c)\mathbf{Y}_{jjm}(\mathbf{r}/r).\tag{6}$$

Note that the normalization is such that

$$\epsilon_0\int\boldsymbol{\mathcal{E}}_{\omega jm}\cdot\boldsymbol{\mathcal{E}}_{\omega'j'm'}{}^*d\mathbf{r}=\tfrac{1}{2}\hbar\omega c\delta(\omega-\omega')\delta_{jj'}\delta_{mm'},$$
$$\int\boldsymbol{\mathcal{E}}_{\omega jm}{}^*\cdot\boldsymbol{\mathcal{E}}_{\omega'j'm'}{}^*d\mathbf{r}=0=\int\boldsymbol{\mathcal{E}}_{\omega jm}\cdot\boldsymbol{\mathcal{E}}_{\omega'j'm'}d\mathbf{r}.\tag{7}$$

Thus, if we expand a given field as

$$\mathbf{E}=\sum_{jm}\int F(\omega jm)\boldsymbol{\mathcal{E}}_{\omega jm}d\omega/c^{1/2}$$
$$+\sum_{jm}\int F^*(\omega jm)\boldsymbol{\mathcal{E}}_{\omega jm}{}^*d\omega/c^{1/2},\tag{8}$$

we see the field energy U is

$$U=\epsilon_0\int E^2d\mathbf{r}=2\epsilon_0\sum_{jm}\sum_{j'm'}\int F(\omega jm)$$
$$\times F^*(\omega'j'm')\boldsymbol{\mathcal{E}}_{\omega jm}\cdot\boldsymbol{\mathcal{E}}_{\omega'j'm'}{}^*d\omega d\omega'd\mathbf{r}/c$$
$$=\sum_{jm}\int\hbar\omega F(\omega jm)F^*(\omega jm)d\omega,\tag{9}$$

which indicates that $F(\omega jm)$ and $F^*(\omega jm)$ are annihilation and creation operators for the (ωjm), photon respectively,

$$(\nu_{\omega jm}|F^*(\omega jm)|\nu_{\omega jm}-1)=(\nu_{\omega jm}/d\omega)^{1/2}$$
$$=(\nu_{\omega jm}-1|F(\omega jm)|\nu_{\omega jm}),\tag{10}$$

where $\nu_{\omega jm}$ is the number of the (ωjm) photon.

The probability of transition $n_1\nu_1\leftrightarrow n_2\nu_2$ is[9]

$$P(n_1\nu_1\leftrightarrow n_2\nu_2)$$
$$=(\pi/\hbar^2)|(n_1\nu_1|H_i|n_2\nu_2)|^2\delta(\omega_{\nu_1\nu_2}-\omega_{n_1n_2}),\tag{11}$$

where n_1 and n_2 are molecular states, ν_1 and ν_2 are photon numbers,

$$\omega_{ab}=(E_a-E_b)/\hbar\tag{12}$$

and

$$H_i=(e/\mu)\sum_i[\mathbf{p}_i\cdot\mathbf{A}_i-\mathbf{s}_i\cdot(\nabla\times\mathbf{A}_i)],\tag{13}$$

where $\mathbf{p}_i$ and $\mathbf{s}_i$ are the momentum and spin of ith electron, respectively. $\mathbf{A}_i$ is the vector potential at the position of ith electron. e and μ are the electron charge and mass, respectively. In H_i the contributions of nuclei are neglected.

In the same way as in (8) we set

$$\mathbf{A}_i=\sum_{jm}\int F(\omega jm)\mathcal{A}_{\omega jm}(\mathbf{r}_i)d\omega/c^{1/2}$$
$$+\sum_{jm}\int F^*(\omega jm)\mathcal{A}_{\omega jm}{}^*(\mathbf{r}_i)d\omega/c^{1/2}\tag{14}$$

[8] A. I. Akhiezer and V. B. Berestetsky, *Quantum Electrodynamics* (izd. Fiz. Mat. Lit, Moscow, 1953) (English transl.: AEC-tr-2876).

[9] See for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), Sec. 43.

in (13). If

$$\nu_1 = \nu - 1, \quad \nu_2 = \nu \qquad (15)$$

in (11), we have

$$P(n_1\nu - 1 \leftrightarrow n_2\nu)$$

$$= (\pi/\hbar^2)(\nu_{\omega_0 jm}^{(\mathrm{mg})}/c)\,|\,(n_1|\,(e/\mu)\sum_i\,[-\mathbf{p}_i\cdot\mathscr{A}_{\omega_0 jm}$$

$$+ \mathbf{s}_i\cdot(\nabla\times\mathscr{A}_{\omega_0 jm})]|n_2)^2, \quad (16)$$

where

$$\omega_0 = \omega_{n_1 n_2} \qquad (17)$$

and $\nu_{\omega_0 jm}^{(\mathrm{mg})}$ is the number of the (magnetic jm) photons with frequency $\omega_0 \sim \omega_0 + d\omega$.

From (6) we see

$$\mathbf{p}_i\cdot\mathscr{A}_{\omega_0 jm} = (\hbar\omega/16\pi^3 c^2 \epsilon_0)^{1/2} e^{-i\omega_0 t} g_j(\omega_0 r_i/c)$$

$$\times r_i^{-2}(\mathbf{r}_i \times \mathbf{Y}_{jjm})\cdot\mathbf{l}_i, \quad (18)$$

where $\mathbf{l}_i$ is the orbital angular momentum of ith particle.

Using formulas

$$g_j r_i^{-2}(\mathbf{r}_i \times \mathbf{Y}_{jjm}) = -\nabla g_j Y_{jm}/[j(j+1)]^{1/2} \quad (19)$$

and

$$\nabla\times g_j \mathbf{Y}_{jjm} = \nabla g_j Y_{jm}[(j+1)/j]^{1/2}, \quad (20)$$

which can be shown from (4) we have

$$-\mathbf{p}_i\cdot\mathscr{A}_{\omega_0 jm} + \mathbf{s}_i\cdot(\nabla\times\mathscr{A}_{\omega_0 jm})$$

$$= (\hbar\omega_0/16\pi^3 c^2 \epsilon_0)^{1/2} e^{-i\omega_0 t}\nabla g_n Y_{jm}$$

$$\cdot[\{j(j+1)\}^{-1/2}\mathbf{l}_i + \{(j+1)/j\}^{1/2}\mathbf{s}_i]. \quad (21)$$

One can define the (magnetic jm) moment as

$$Q_{jm}^{(\mathrm{mg})} = (e/\mu)[(2j+1)/4\pi]^{1/2}(2j-1)!(i\omega_0/c)^{-j}$$

$$\times\sum_i (\nabla g_j Y_{jm})_i\cdot[(j+1)^{-1}\mathbf{l}_i + \mathbf{s}_i]$$

$$\cong (e/\mu)[4\pi/(2j+1)]^{1/2}$$

$$\times\sum_i (\nabla r_i^j Y_{jm})\cdot[(j+1)^{-1}\mathbf{l}_i + \mathbf{s}_i], \quad (22)$$

where the last expression is obtained when

$$\omega_0 r_i/c \ll 1, \qquad (23)$$

so that

$$g_j(\omega_0 r/c) \cong 4\pi(i\omega_0 r/c)^j/(2j+1)!. \quad (24)$$

Note that

$$Q_{10}^{(\mathrm{mg})} = (e/\mu)\sum_i (l_{iz} + 2s_{iz}), \qquad (25)$$

which is the familiar magnetic dipole moment.

From (21) and (22) we see

$$\sum_i [-\mathbf{p}_i\cdot\mathscr{A}_{\omega_0 jm} + \mathbf{s}_i\cdot(\nabla\times\mathscr{A}_{\omega_0 jm})](e/\mu)$$

$$= [(j+1)/j(2j+1)]^{1/2}[(2j-1)!]^{-1}$$

$$\times e^{-i\omega_0 t}(i\omega_0/c)^j Q_{jm}^{(\mathrm{mg})}/2\pi c. \quad (26)$$

Thus, from (16) the probability of the (magnetic jm) moment transition is

$$P_{jm}^{(\mathrm{mg})}(n_1 \rightarrow n_2)$$

$$= (j+1)[j(2j+1)\{(2j-1)\}^2]^{-1}\nu_{\omega_0 jm}^{(\mathrm{mg})}\omega_0^{2j+1}$$

$$\times(4\pi c^{2j+3}\hbar\epsilon_0)^{-1}|\,(n_1|Q_{jm}^{(\mathrm{mg})}|n_2)|^2. \quad (27)$$

ELECTRIC MULTIPOLE TRANSITION

The electric multipole transition can be discussed in the similar way. Since it is not the main purpose of the present paper, we will just show the result.

The only difference is to start with a photon wave function which is the eigenfunction of the total angular momentum and energy with eigenvalues j, m, and $\hbar\omega$, while the parity is $(-1)^j$, instead of $(-1)^{j+1}$.

The (electric jm) moment is defined as

$$Q_{jm}^{(\mathrm{el})} = \sum_i e_i[4\pi/(2j+1)]^{1/2} r_i^j Y_{jm}, \qquad (28)$$

where we should include both electrons and nuclei in the summation, and e_i is the charge of ith particle. This definition gives

$$Q_{10}^{(\mathrm{el})} = \sum_i e_i z_i, \qquad (29)$$

which is the familiar electric dipole moment.

The transition probability is

$$P_{jm}^{(\mathrm{el})}(n_1 \leftrightarrow n_2)$$

$$= j(j+1)[(2j+1)\{(2j-1)!\}^2]^{-1}\nu_{\omega_0 jm}^{(\mathrm{el})}\omega_0^{2j+1}$$

$$\times(4\pi c^{2j+1}\hbar\epsilon_0)^{-1}|\,(n_1|Q_{jm}^{(\mathrm{el})}|n_2)|^2. \quad (30)$$

Since the matrix element of $Q_{jm}^{(\mathrm{mg})}$ is about $(e/\mu)r_0^{j-1}\hbar$ as seen from (22), while that of $Q_{jm}^{(\mathrm{el})}$ is about er_0^j as seen from (28), taking r_0 for the atomic dimension, we obtain the order of magnitude of $P_{jm}^{(\mathrm{mg})}$ by means of $P_1^{(\mathrm{el})}$ as

$$P_{jm}^{(\mathrm{mg})} = (\omega_0^{j-1}r_0^{j-2}\hbar/c^j\mu)^2(\nu_{\omega_0 jm}^{(\mathrm{mg})}/\nu_{\omega_0 1}^{(\mathrm{el})})P_1^{(\mathrm{el})}. \quad (31)$$

SPIN-ORBIT ELECTRIC OR MAGNETIC DIPOLE TRANSITION

The conventional theory of $\Delta S = \pm 1$ transition is to take into account the effect of the spin-orbit interaction

$$H_{\mathrm{so}} = -i(e\hbar/2\mu^2 c^2)\sum_i \mathbf{s}_i\cdot(\mathbf{E}\times\nabla)_i. \qquad (32)$$

Since this interaction is similar to $Q_{2ms}^{(\mathrm{mg})}$, which is given by (33), it can connect a singlet to a triplet. Thus,

$$|a00) + \sum_{c,M_s} (c1M_S|H_{\mathrm{so}}|a00)(E_a - E_c)^{-1}|c1M_S)$$

$$|b1M_S) + \sum_d (d00|H_{\mathrm{so}}|b1M_S)(E_b - E_d)^{-1}|d00)$$

$$\qquad\qquad (33)$$

are the improved wave functions of the initial and the final states. The electric dipole transition for $a \leftrightarrow b$ is

thus from (30)

$$P_{1ms0}^{(el)} = (\nu_{\omega01m}^{(el)}\omega_0^2/6\pi c^3\hbar^2 c_0)$$

$$\times |\sum_{c,M_s} (a00|H_{so}|c1M_S)(E_a-E_c)^{-1}$$

$$\times (c|Q_{1m}^{(el)}|b) + \sum_{d,M_s} (d00|H_{so}|b1M_S)$$

$$\times (E_b-E_d)^{-1}(a|Q_{1m}^{(el)}|d)|^2. \quad (34)$$

Since the order of magnitude of the electric field E is (electric energy)/r_0 or $\mu\omega_0^2 r_0$, we see the order of magnitude of the matrix element of H_{so} is $\hbar\omega_0/\mu c^2$ as expected from the fact that the spin-orbit interaction appears as a relativistic correction. Thus, the transition probability due to this mechanism is

$$P_{1\,so}^{(el)} \cong (\hbar\omega_0/\mu c^2)^2 P_1^{(el)}. \quad (35)$$

From (31) we see that the spontaneous emission probability through the magnetic quadrupole transition, which is $P_2^{(mg)}$ with $\nu=1$, gives exactly the same expression as (35).

In some cases the electric dipole transition is still forbidden and only the magnetic dipole transition can appear with the spin-orbit coupling. The transition probability for such case has the order of magnitude given by

$$P_{1\,so}^{(mg)} \cong (\hbar\omega_0/\mu c^2)^2 P_1^{(mg)}. \quad (36)$$

From (31) we see

$$P_3^{(mg)} = (\omega_0^2 r_0^2/c^2)^2 P_1^{(mg)}$$
$$= (\omega_0\mu\omega_0 r_0^2/\mu c^2)^2 P_1^{(mg)}$$
$$\cong (\hbar\omega_0/\mu c^2)^2 P_1^{(mg)}, \quad (37)$$

which shows that the magnetic octupole transition is as important as the spin-orbit magnetic dipole transition.

Somehow the magnetic multipole transition has never been discussed, but it should be as important as the spin-orbit electric or magnetic dipole transition for $\Delta S = \pm 1$ transitions.

MAGNETIC QUADRUPOLE MOMENT

From (22) with $j=2$ we obtain the five components of the magnetic quadrupole moment. They are

$$Q_{2m}^{(mg)} = Q_{2ml}^{(mg)} + Q_{2ms}^{(mg)}, \quad (38)$$

$$Q_{2ms}^{(mg)} = (e/\mu)\sum_i [q_{iz}^{2m}s_{iz} + \tfrac{1}{2}q_{i+}^{2m}(s_{ix}+is_{iy})$$

$$+ \tfrac{1}{2}q_{i-}^{2m}(s_{ix}-is_{iy})], \quad (39)$$

while $Q_{2ml}^{(mg)}$ is obtained by replacing $\mathbf{s}$ by $\mathbf{l}/3$ in (33). Coefficients q's are tabulated in Table I.

Let us assume a two-electron system. Such system can be either a triplet or a singlet, if we neglect the spin-orbit interaction. The wave function of each state is a product of the orbital part and the spin part which can

TABLE I. Coefficients q^{2m}.

m	q_z^{2m}	q_+^{2m}	q_-^{2m}
-2	0	0	$-6^{1/2}(x-iy)$
-1	$(3/2)^{1/2}(x-iy)$	0	$-6^{1/2}z$
0	$2z$	$x-iy$	$-x-iy$
1	$(3/2)^{1/2}(x+iy)$	$6^{1/2}z$	0
2	0	$6^{1/2}(x+iy)$	0

be designated as $|\xi SM_S)$. It is easy to see that

$$(a00|q_{1z}^{2m}s_{1z}+q_{2z}^{2m}s_{2z}|b10)=(\hbar/2)(a|q_{1z}^{2m}-q_{2z}^{2m}|b),$$

$$(a00|q_{1+}^{2m}s_{1+}+q_{2+}^{2m}s_{2+}|b1-1)$$
$$=(\hbar/2)(a|q_{1+}^{2m}-q_{2+}^{2m}|b), \quad (40)$$

$$(a00|q_{1-}^{2m}s_{1-}+q_{2-}^{2m}s_{2-}|b11)=(\hbar/2)(a|q_{1-}^{2m}-q_{2-}^{2m}|b),$$

are the only finite matrix elements. We see that these matrix elements are not generally zero because the orbital part of the wave function $|a)$ and $|b)$ are symmetric and antisymmetric, respectively, under the exchange of two electrons. Since, as shown by Mizushima and Koide,[6] the corresponding matrix elements of all the electric multipole moments and the magnetic dipole moment are zero, the magnetic quadrupole moment is the lowest moment which has finite matrix elements between states with different total spin.

If we assume that

$$|a)=N[u(1)v(2)+v(1)u(2)],$$
$$|b)=N'[u'(1)v'(2)-v'(1)u'(2)], \quad (41)$$

where

$$N^{-2}=2\left[1+\left\{\int u(1)v(1)d\mathbf{r}_1\right\}^2\right],$$

$$N'^{-2}=2\left[1-\left\{\int u'(1)v'(1)d\mathbf{r}_1\right\}^2\right], \quad (42)$$

we obtain

$$(a|q_1-q_2|b)$$
$$=2NN'[(v|v')(u|q|u')-(u|u')(v|q|v')$$
$$+(u|v')(v|q|u')-(v|u')(u|q|v')]. \quad (43)$$

MAGNETIC OCTUPOLE MOMENT

The magnetic octupole moment $Q_{3m}^{(mg)}$ can also be divided into two parts:

$$Q_{3m}^{(mg)} = Q_{3ml}^{(mg)} + Q_{3ms}^{(mg)}, \quad (44)$$

$$Q_{3ms}^{(mg)} = (e/\mu)\sum_i [q_{iz}^{3m}s_{iz} + \tfrac{1}{2}q_{i+}^{3m}(s_{ix}+is_{iy})$$

$$+ \tfrac{1}{2}q_{i-}^{3m}(s_{ix}-is_{iy})], \quad (45)$$

while $Q_{3ml}^{(mg)}$ is obtained by replacing $\mathbf{s}$ by $\mathbf{l}/4$ in (45).

Coefficients q's are tabulated in Table II.

For the matrix elements we see that formulas (40) and (43) holds for q^{3m}.

TABLE II. Coefficients q^{3m}.

m	q_z^{3m}	q_+^{3m}	q_-^{3m}
-3	0	0	$-(45/4)^{1/2}(x-iy)^2$
-2	$(15/8)^{1/2}(x-iy)^2$	0	$-30^{1/2}z(x-iy)$
-1	$12^{1/2}z(x-iy)$	$(45/4)^{1/2}(x-iy)^2$	$-3^{1/2}(3z^2-r^2)$
0	$(9z^2-3r^2)/2$	$3z(x-iy)$	$-3z(x+iy)$
1	$12^{1/2}z(x+iy)$	$3^{1/2}(3z^2-r^2)$	$-(45/4)^{1/2}(x+iy)^2$
2	$(15/8)^{1/2}(x+iy)^2$	$30^{1/2}z(x+iy)$	0
3	0	$(45/4)^{1/2}(x+iy)^2$	0

HYDROGEN MOLECULE

The lowest triplet state of the hydrogen molecule is a dissociative state $^3\Sigma_u^+$. Since it is a dissociative state the lifetime of this state due to the spontaneous emission cannot be measured. The calculation in this section is just to show that the magnetic quadrupole transition can be much greater than the spin-orbit electric dipole transition.

The Heitler-London wave function[9] is well known to give a good approximation for the ground state $^1\Sigma_g^+$ and the lowest triplet state $^3\Sigma_u^+$. A large number of better wave functions are proposed for these states,[9] but for the present purpose of rough estimation the Heitler-London wave function will be good enough.

The Heitler London wave functions are obtained by identifying

$$u(i)=u'(i)=\psi_{1s}(r_{ai}),$$
$$v(i)=v'(i)=\psi_{1s}(r_{bi}), \tag{46}$$

where r_{ai} and r_{bi} are distances between the ith electron and the protons a and b, respectively, and ψ_{1s} is the hydrogen wave function. From Table I it is easy to see that the only finite matrix elements of the magnetic quadrupole moment are

$$(^1\Sigma_g^+00|Q_{20}^{(mg)}|^3\Sigma_u^+10)=4(e\hbar/2\mu)N_+N_-r_{ab},$$
$$(^1\Sigma_g^+00|Q_{21}^{(mg)}|^3\Sigma_u^+1-1)=24^{1/2}(e\hbar/2\mu)N_+N_-r_{ab}, \tag{47}$$
$$(^1\Sigma_g^+11|Q_{2-1}^{(mg)}|^3\Sigma_u^+11)=24^{1/2}(e\hbar/2\mu)N_+N_-r_{ab},$$

where r_{ab} is the internuclear distance. With the approximation of $N_+=N_-=2^{-1/2}$ we obtain

$$P_{20}^{(mg)}(^1\Sigma_g^+ \leftrightarrow {}^3\Sigma_u^+0)$$
$$= (2/15)\nu\omega_0^5(4\pi c^7\hbar\epsilon_0)^{-1}(e\hbar/2\mu)^2r_{ab}^2,$$
$$P_{2\pm1}^{(mg)}(^1\Sigma_g^+ \leftrightarrow {}^3\Sigma_u^+\pm1) \tag{48}$$
$$= 5^{-1}\nu\omega_0^5(4\pi c^7\hbar\epsilon_0)^{-1}(e\hbar/2\mu)^2r_{ab}^2,$$

which shows that the magnetic quadrupole transition is more effective as the internuclear distance increases, as far as $\omega_0 r_{ab}<c$.

For the spin-orbit interaction one can divide the electric field $\mathbf{E}$ into two parts: The part due to the nucleus to which the electron under consideration is attached and the part due to the other atom. Assuming that the charge distribution is spherical around the other atom we have,

$$\mathbf{E}=\mathbf{E}_a+\mathbf{E}_b=(d\Phi_a/dr_{ai})\mathbf{r}_{ai}/r_{ai}+(d\Phi_b/dr_{bi})\mathbf{r}_{bi}/r_{bi}, \tag{49}$$

where ψ_a and Φ_b are potentials due to each part mentioned above. Now

$$\mathbf{r}_{ai}\times\nabla=(i/\hbar)\mathbf{l}_{ai}, \quad \mathbf{r}_{bi}\times\nabla=(i/\hbar)\mathbf{l}_{ai}+\mathbf{r}_{ba}\times\nabla, \tag{50}$$

where $\mathbf{l}_{ai}$ is the orbital angular momentum of the ith electron with respect to the nucleus a.

Using (46) we have

$$\mathbf{l}_{ai}u(i)=0, \tag{51}$$

while

$$(1s|\mathbf{r}_{ba}\times\nabla|2p_x)=(16/2^{1/2}27)(r_{ba}/r_B)\mathbf{j},$$
$$(1s|\mathbf{r}_{ba}\times\nabla|2p_y)=-(16/2^{1/2}27)(r_{ba}/r_B)\mathbf{i}, \tag{52}$$

where $\mathbf{i}$ and $\mathbf{j}$ are unit vectors along the x and y axes, respectively, and r_B is the Bohr radius.

If the orbital part of the wave function of the $^1\Pi_u(1s2p\pi)$ state is

$$|^1\Pi_u)=[\psi_{1s}(1)\psi_{2p\pi}(2)+\psi_{1s}(2)\psi_{2p\pi}(1)]/2^{1/2}, \tag{53}$$

we find

$$(^1\Pi_{u\pm}|H_{so}|^3\Sigma_u^+1\pm1)$$
$$= (4/27)(e\hbar/2\mu^2)(d\Phi_b/dr_b)r_b^{-1}(r_{ba}/r_B)(\hbar/2)$$
$$= (Z/27\pi\epsilon_0)(e\hbar/2\mu c)^2(r_{ab}^2r_B)^{-1}, \tag{54}$$

where Z is effective charge of the second atom for the electron in the first atom. Z is less than one and goes to zero as r_{ab} increases. Since

$$(^1\Pi_{u\pm}|Q_{1\pm1}^{(el)}|^1\Sigma_g^+)=(2^8/3^6)r_Be, \tag{55}$$

we see from (34) that

$$p_{1\pm1\,so}^{(el)}=(Z^2/10^7)\nu\omega_0^3e^6\hbar^3(\mu^4c^7\epsilon_0^3)^{-1}(\Delta r_{ab}^2)^{-2}, \tag{56}$$

where

$$\Delta=E(^1\Pi_u)-E(^3\Sigma_u^+). \tag{57}$$

In obtaining this formula we assumed that the main contributions come from the mixing of the $^1\Pi_u(1s2p\pi)$ state to the $^3\Sigma_u^+$ state. Note that formula (56) shows that the transition probability in this case decreases as r_{ab} increases as $(Z/r_{ab}^2)^2$.

By comparing (56) to (48) we see

$$P_2^{(mg)}/P_{1\,so}^{(el)}$$
$$= (10/Z^2)(\hbar\omega_0/Rch)^2(\Delta/Rch)^2(r_{ab}/r_B)^6, \tag{58}$$

where R is the Rydberg constant. In our case

$$Z^2\sim1/10,$$
$$\hbar\omega_0/Rch\approx1/2,$$
$$\Delta/Rch\sim1/4, \tag{59}$$
$$r_{ab}/r_B=1.4,$$

at the equilibrium distance of the ground state. Thus the above ratio is about 10 in favor of the magnetic quadrupole transition over the conventional spin-orbit electric dipole transition. When the internuclear distance r_{ab} increases the ratio will increase very rapidly.

SELECTION RULES

The two comparative mechanisms, the magnetic quadrupole transition and the spin-orbit electric dipole transition have slightly different selection rules. For the case of $\Delta S = \pm 1$ transitions which we are interested in here the selection rules for the magnetic quadrupole transition are just like those of the electric dipole transition, or

$$\Delta L = 0, \pm 1, \text{ but } L = 0 \leftrightarrow 0; \text{ parity change}, \quad (60)$$

while those for the spin-orbit electric dipole transition are

$$\Delta L = 0, \pm 1, \pm 2; \text{ parity change}, \quad (61)$$

in the case of atoms with L-S coupling. Thus, for example, $^1S \leftrightarrow {}^3S$ and $^2S \leftrightarrow {}^4D$ transitions can only be explained by the spin-orbit electric dipole transition.

Transitions with parity no change cannot be explained by either of them, and we have to go to the magnetic octupole transition or the spin-orbit magnetic dipole transition. Their selection rules for $\Delta S = \pm 1$ transitions are

$$\Delta L = 0, \pm 1, \pm 2, \text{ but } L = 0 \leftrightarrow 0;$$
$$\text{parity no change for magnetic octupole}, \quad (62)$$

$$\Delta L = 0, \pm 1, \pm 2; \text{ parity no change for}$$
$$\text{spin-orbit magnetic dipole}. \quad (63)$$

Selection rules for molecules can be found by finding those for the electric dipole and the electric quadrupole transitions. The selection rules for the magnetic quadrupole and the magnetic octupole transitions are the same as those respectively. For the benzene molecule, for example, the lowest triplet state $^3B_{1u}$ is known to be able to go to the ground state $^1A_{1g}$ by the spin-orbit electric dipole transition[5,6] but we see that the magnetic quadrupole transition is forbidden for this transition. In the case of the naphthalene and anthracene molecules, on the other hand, the lowest triplet state is assumed[10] to be $^3B_{2u}$, and the magnetic quadrupole transition is allowed from this state to the ground state $^1A_{1g}$. The lowest triplet state of the benzene molecule is observed[11] to have the lifetime of more than 300 sec, while in most aromatic molecules the triplet lifetime is accepted to be about 1 sec. This may be explained by the above conclusion, since our analysis on the hydrogen molecule showed that the magnetic quadrupole transition must be more important than the spin-orbit electric dipole transition in the case of large molecules.

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Absolute Electron Excitation Cross Sections of Helium*

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The absolute apparent electron excitation functions of helium have been measured for the $3\,^1S$, $4\,^1S$, $5\,^1S$, $6\,^1S$, $3\,^1P$, $4\,^1P$, $3\,^1D$, $4\,^1D$, $5\,^1D$, $6\,^1D$, $3\,^3S$, $4\,^3S$, $5\,^3S$, $3\,^3P$, $3\,^3D$, $4\,^3D$, $5\,^3D$, and $6\,^3D$ states at pressures sufficiently low so that the effects of radiation imprisonment and collisional excitation transfer can be neglected. Corrections due to polarization of the radiation and the cascading from the upper excited states have been applied to the experimental data and the true excitation functions obtained. The peak values and the shape of these excitation functions are compared with the results reported from other laboratories. Generally good agreement is found with the previous works where the collisional excitation transfer was properly reduced and allowance was made for the cascading effect. The experimental cross sections show satisfactory agreement with the theoretical values calculated by the Born approximation for the ^1S and ^1P states at high-electron energies, but are about four times larger than the theoretical values for ^1D states. In the case of the triplet series, the experimental cross sections exceed the calculated values by factors of ten to one hundred or more. It is concluded that the population of the triplet states is produced mainly by processes other than direct excitation.

I. INTRODUCTION

RECENT studies of electron excitation of helium atoms indicate that some of the atomic states may be populated to a large extent by collisional excitation transfer and cascading in addition to the usual electron-impact excitation process.[1,2] The excitation transfer and its concomitant effect on cascading may be reduced and even eliminated if measurements of the excitation are made with the helium gas at low pressure, i.e., about $1\,\mu$ or less. Furthermore the populations of the ^1P states are affected by imprisonment of resonance radiation at pressures above a few tenths of a micron and therefore

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