Energy Levels, Selection Rules, and Line Intensities for Molecular Beam Electric Resonance Experiments with Diatomic Molecules*

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(Received April 24, 1950)

In the molecular beam electric resonance method the energy levels in an electric field of a diatomic molecule which is in the ground electronic state, and a low vibrational and rotational state are studied. Transitions are produced between states with different space quantization of the molecule relative to the electric field and with different couplings of the angular momenta of the nuclei and of the molecular rotation. Thus the interaction of the molecule with the field and the internal molecular interactions (e.g., nuclear electrical quadrupole interactions and nuclear spin—molecular orbit interactions) are measured. In this paper we give the stationary state energy values and eigenfunctions for "very weak," "weak," and "strong" field conditions for a diatomic molecule in which one nucleus has a spin of $\frac{1}{2}$. Selection rules for the transitions are developed and some considerations on line intensities are discussed. Finally, there is presented the theory of double quantum transitions, which are predicted to occur at one-half the frequency given by the Bohr condition, $\Delta W = h\nu$, provided the radiofrequency field is sufficiently intense.

I. INTRODUCTION

RECENT experiments[1,2] by the molecular beam electric resonance method[3,4] of observing the energy levels of polar diatomic molecules have raised a number of questions related to selection rules and intensities for the spectra observed. In essence the method consists in selecting for study a single rotational (usually $J=1$ and occasionally $J=2$) and orientational state of a diatomic molecule in an electric field. This selection can be made because the force which an inhomogeneous electric field exerts on a molecule is dependent upon its rotational state and upon the orientation of its rotational angular momentum with respect to the field direction. The scheme employed is the familiar one of allowing the molecules to pass through two inhomogeneous electric fields, designated as the A and B-fields, which will produce equal and opposite deflections only for molecules in a single rotational and orientational state. Hence only these molecules will impinge upon the suitably placed detector.[5]

A study of the energy levels of these molecules in an electric field is made by inserting a homogeneous electric field, designated as the C-field, between the A and B-fields and impressing a radiofrequency field also in this region. At appropriate frequencies, ordinarily in the megacycle range, transitions are induced which bring the molecules to other energy states. In these different states the molecules will have different internal energies and (or) different interactions with the external field, but their rotational angular momentum and, of course, their nuclear spins will be unchanged. If the

molecule which has been subjected to a transition in the C-field arrives in the B-field in a different state than it would have had if it had not suffered the transition, and, furthermore, if in this different state it is subjected to a different force in the B-field, then the transition will be observed as a change in the intensity of the molecular beam which strikes the detector.

The Hamiltonian for a polar diatomic molecule in an electric field should include a term for the interaction of the field with the electric dipole moment, terms for the electrical quadrupole interactions associated with the nuclei, terms for the spin-orbit coupling between each nuclear spin and the molecular rotational angular momentum, and, finally, the magnetic dipole-dipole interaction between the two nuclei. The energy levels are studied for field intensities ranging in value from those for which the field interaction term is negligibly small relative to the smallest internal interactions observed (~ 10 kc/sec.) to those for which the field interaction is large ($\sim$ several hundred megacycles) relative to the electrical quadrupole interactions. It will be convenient to distinguish several special cases characterized by the relative magnitude of the field interaction and the internal molecular interactions.

Thus far electric resonance experiments have been performed primarily with alkali fluoride molecules.[6] These molecules are especially simple because there is only an electrical quadrupole interaction associated with the alkali nucleus, since the spin of the fluorine nucleus is $\frac{1}{2}$. This paper will be restricted to the case in which the molecule has only one electrical quadrupole interaction. Still, it will be seen that many of the results can be rather simply extended to the case in which there are two electrical quadrupole interactions, but one of them is much smaller than the other. An extension to the more general case of two electrical quadrupole interactions of arbitrary magnitude can be made

* This research has been supported in part by the ONR.
[1] L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).
[2] V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).
[3] H. K. Hughes, Phys. Rev. **72**, 614 (1947).
[4] J. W. Trischka, Phys. Rev. **74**, 718 (1948).
[5] A majority of the molecules in the higher rotational states are deflected only a very small amount by the inhomogeneous fields and can most easily be prevented from reaching the detector by the use of a wire stop.

[6] Recently experiments have been performed with TlCl³⁵. See Lee, Carlson, Fabricand, and Rabi, Phys. Rev. **78**, 340A (1950).

with the help of the results of Bardeen and Townes, and of Racah.[7]

The second section of this paper will give the energy values and the eigenfunctions for several cases characterized by the magnitude of the field interaction. In the third section we shall present the selection rules which will apply for stimulated transitions in these various cases. Line intensities will be discussed in the fourth section. In this connection an important consideration is the correspondence that exists between states at low fields and states at high fields, assuming adiabatic change of the field parameter.

A condition is sometimes realized under very weak field conditions for which the intensity of the radiofrequency field is larger than that of the static field. Hence the field free state must be considered to be perturbed primarily by the radiofrequency field rather than by the static field. It turns out that in such a situation a two quantum transition is predicted. This matter is discussed in the final section of this paper.

II. STATIONARY STATE ENERGY VALUES AND EIGENFUNCTIONS

The most general Hamiltonian which it has been necessary to assume for the alkali fluoride molecule in an electric field is:

$$H = \frac{\hbar^2}{2A}\mathbf{J}^2 - \mathbf{\mu}\cdot\mathbf{E} - eq_1Q_1\frac{\{3(\mathbf{I}_1\cdot\mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_1\cdot\mathbf{J}) - I_1^2\mathbf{J}^2\}}{2I_1(2I_1-1)(2J-1)(2J+3)}$$

$$+ c_1(\mathbf{I}_1\cdot\mathbf{J}) + c_2(\mathbf{I}_2\cdot\mathbf{J}) + \frac{g_1g_2\mu_N^2}{r^3}$$

$$\times\frac{[3(\mathbf{I}_1\cdot\mathbf{J})(\mathbf{I}_2\cdot\mathbf{J}) + 3(\mathbf{I}_2\cdot\mathbf{J})(\mathbf{I}_1\cdot\mathbf{J}) - 2(\mathbf{I}_1\cdot\mathbf{I}_2)J(J+1)]}{(2J+3)(2J-1)}.$$

The first term in which $\mathbf{J}$ is the rotational angular momentum and A is the moment of inertia, is the rotational energy term. The second term gives the interaction of the external electric field $\mathbf{E}$ with the permanent electric dipole moment of the molecule. The third term is the electrical quadrupole interaction between the electrical quadrupole moment of the alkali nucleus, Q_1, and a second derivative of the electric potential at the position of the alkali nucleus, q_1, produced by the remaining charges in the molecule. q_1 and Q_1 are defined in reference 7a. Here e is the proton charge. (The subscript 1 refers to the alkali nucleus.) $\mathbf{I}_1$ is the spin of the alkali nucleus. There is no electrical quadrupole interaction with the F nucleus because its spin is $\frac{1}{2}$. This form of the electrical quadrupole interaction operator gives only the matrix elements diagonal[8] in J. The fourth and fifth terms are cosine couplings between the nuclear spins (F spin designated by $\mathbf{I}_2$) and the rotational angular momentum of the molecule. c_1 and c_2 are constants. The last term is the magnetic dipole-dipole interaction between the alkali and F nuclei, for which r is the internuclear distance, g_1 and g_2 are the gyromagnetic ratios for the alkali and F nuclei respectively, and μ_N is one nuclear magneton.[9]

In general it will be true that $\hbar^2/2A \gg eq_1Q_1 \gg (c_2$ or c_1 or $g_1g_2\mu_N^2/r^3)$. We distinguish three cases which are of interest experimentally:

$$\mu^2E^2/(\hbar^2/2A) \ll c_2 \quad \text{or} \quad g_1g_2\mu_N^2/r^3$$
$$\text{("very weak" field)} \quad (1)$$

$$(c_2 \text{ or } g_1g_2\mu_N^2/r^3) \ll \mu^2E^2/(\hbar^2/2A) \ll eq_1Q_1$$
$$\text{("weak" field)} \quad (2)$$

$$eq_1Q_1 \ll \mu^2E^2/(\hbar^2/2A) \ll \hbar^2/2A \quad \text{("strong" field)} \quad (3)$$

(A) Very Weak Field Case

The energy eigenvalues and eigenfunctions for the very weak field case are given in the literature.[10,11] The energy values are:

$$W_{J,\,I_1,\,F_1,\,I_2,\,F=F_1\pm\frac{1}{2},\,M} = \frac{\hbar^2}{2A}J(J+1) - \frac{eq_1Q_1}{(2J-1)(2J+3)(2I_1)(2I_1-1)}\{\tfrac{3}{4}K_1(K_1+1) - I_1(I_1+1)J(J+1)\}$$

$$+ \frac{c_1K_1}{2} \pm c_2\frac{F_1(F_1+1) + J(J+1) - I_1(I_1+1)}{4F_1(F_1+1)}(F_1+\tfrac{1}{2}\mp\tfrac{1}{2}) + \frac{g_1g_2\mu_N^2}{r^3(2J+3)(2J-1)}\{3K_1g - 2J(J+1)D'\}\frac{K}{2}$$

$$+ \frac{\alpha^2\hbar^2\left[3(M^2+\frac{1}{4}) - F_1(F_1+1)\mp\dfrac{6M^2}{2F_1+1}\right][3D(D-1) - 4F_1(F_1+1)J(J+1)]}{2J(J+1)(2J-1)(2J+3)2F_1(F_1+1)(2F_1-1)(2F_1+3)}$$

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[7] a J. Bardeen and C. H. Townes, Phys. Rev. 73, 97 (1948); b G. Racah, Phys. Rev. 62, 438 (1942).

[8] H. B. G. Casimir, On the Interaction between Atomic Nuclei and Electrons (Teyler's Tweede Genootschap, 1936).

[9] J. M. B. Kellogg et al., Phys. Rev. 57, 677 (1940). It is shown that the spi-spin onperator can be written in this form.

[10] Nierenberg, Rabi, and Slotnick, Phys. Rev. 73, 1430 (1948). Note that the term involving the field is different in this paper. Communication with W. Nierenberg established that a misprint was present in the reference.

[11] Reference given in reference 4. Note that the sign in front of the second term in the bracket differs from that of the reference.

in which

$$\mathbf{F}_1 = \mathbf{I}_1 + \mathbf{J}; \quad \mathbf{F} = \mathbf{F}_1 + \mathbf{I}_2; \quad K_1 = F_1(F_1+1) - I_1(I_1+1) - J(J+1)$$

$$g = \frac{F_1(F_1+1) + J(J+1) - I_1(I_1+1)}{2F_1(F_1+1)}; \quad D = F_1(F_1+1) + J(J+1) - I_1(I+1)$$

$$D' = \frac{F_1(F_1+1) + I_1(I_1+1) - J(J+1)}{2F_1(F_1+1)}; \quad K = F(F+1) - F_1(F_1+1) - I_2(I_2+1)$$

$$\alpha = \mu E / (\hbar^2/2A).$$

The zeroth order eigenfunctions are characterized by the quantum numbers (J, I_1, F_1, I_2, F, M) and will be denoted $\phi(J, I_1, F_1, I_2, F, M)$. Terms 1, 3, and 4 of the Hamiltonian are diagonal in this representation. The contribution of terms 5 and 6 was computed by first-order perturbation theory which neglected off-diagonal elements connecting different F_1 states. The $-\mathbf{\mu} \cdot \mathbf{E}$

interaction has no diagonal matrix elements in this representation, and its contribution was computed by second order perturbation theory.

(B) Weak Field Case

For the weak field case the energy values are:[12]

(a) for $|m_{F_1} + m_2| \neq 0$

$$W_{J, I_1, F_1, m_{F_1} I_2,, m_2} = \frac{\hbar^2}{2A} J(J+1) - \frac{eq_1Q_1}{(2J-1)(2J+3)2I_1(2I_1-1)} \{\tfrac{3}{4}K_1(K_1+1) - I_1(I_1+1)J(J+1)\} + \frac{c_1K_1}{2}$$

$$- \frac{\alpha^2\hbar^2}{2A} \frac{[3m_{F_1}^2 - F_1(F_1+1)][3D(D-1) - 4F_1(F_1+1)J(J+1)]}{2J(J+1)(2J-1)(2J+3)2F_1(F_1+1)(2F_1-1)(2F_1+3)} + c_2 m_2 m_{F_1} g$$

$$+ \frac{g_1 g_2 \mu_N^2}{r^3(2J+3)(2J-1)} \left[\frac{3}{2} \frac{m_2 m_{F_1} D}{F_1(F_1+1)} - \frac{m_2 m_{F_1} D' J(J+1)}{F_1(F_1+1)} \right]$$

(b) for $|m_{F_1} + m_2| = 0$

$$W_{J, I_1, F_1, |\frac{1}{2}|, I_2, |\frac{1}{2}|} = \frac{\hbar^2}{2A} J(J+1) - \frac{eq_1Q_1}{(2J-1)(2J+3)2I_1(2I_1-1)} \{\tfrac{3}{4}K_1(K_1+1) - I_1(I_1+1)J(J+1)\} + \frac{c_1K_1}{2}$$

$$- \frac{\alpha^2\hbar^2}{2A} \frac{[3m_{F_1}^2 - F_1(F_1+1)][3D(D-1) - 4F_1(F_1+1)J(J+1)]}{2J(J+1)(2J-1)(2J+3)2F_1(F_1+1)(2F_1-1)(2F_1+3)} \pm \frac{c_2}{2}(F_1 + \tfrac{1}{2} \mp \tfrac{1}{2})g$$

$$\pm \frac{g_1 g_2 \mu_N^2}{r^3(2J+3)(2J-1)} (F_1 + \tfrac{1}{2} \mp \tfrac{1}{2}) \left[\frac{3}{4} \frac{K_1 D}{F_1(F_1+1)} - \frac{J(J+1)D'}{2F_1(F_1+1)} \right],$$

in which m_{F_1} is the projection of $\mathbf{F}_1$ on the field direction and m_2 is the projection of $\mathbf{I}_2$ on the field direction. The zeroth-order eigenfunctions are for case (a) characterized by the quantum numbers $(J, I_1, F_1, m_{F_1}, I_2, m_2)$ and will be denoted by $\phi(J, I_1, F_1, m_{F_1}, I_2, m_2)$. The eigenfunctions for case (b) have the quantum numbers $(J, I_1, F_1, |m_{F_1}| = \tfrac{1}{2}, I_2, |m_2| = \tfrac{1}{2})$ and are:

$$[\phi(J, I_1, F_1, \tfrac{1}{2}, I_2, -\tfrac{1}{2}) + \phi(J, I_1, F_1, -\tfrac{1}{2}, I_2, +\tfrac{1}{2})]/\sqrt{2}$$

and

$$[\phi(J, I_1, F_1, \tfrac{1}{2}, I_2, -\tfrac{1}{2}) - \phi(J, I_1, F_1, -\tfrac{1}{2}, I_2, +\tfrac{1}{2})]/\sqrt{2}.$$

(The first eigenfunction corresponds to the energy term with the upper signs.) With regard to the approximation involved in our result the same remarks apply for terms 1 to 4 as were made for the very weak field

case. In the computation of the energy contribution of terms 5 and 6 first-order perturbation theory was employed and thus off-diagonal elements connecting different F_1 and m_{F_1} states were neglected.

(C) Strong Field Case[13]

The energy values are:

[12] This computation is readily made if we use the results of U. Fano, J. Research Nat. Bur. Stand. **40**, 215 (1948) and the well-known matrix elements for angular momenta. (E. U. Condon and G. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), Chapter III.)

[13] Reference cited in reference 10 contains solution to this case without the inclusion of the magnetic dipole-dipole interaction. Note that an omission appeared in formula (12) of the reference. The square sign (i.e., raise to power 2) is missing from the first set of inner brackets following the $\pm$ sign.

(a) For $|m_J| \neq 1$ or for $|m_J| = 1$ and $|m_J + m_1| = I_1$ or $I_1 + 1$

$$W_{J, I_1, I_2, m_J, m_1, m_2} = \frac{\hbar^2}{2A}J(J+1) + \frac{\hbar^2}{2A}\alpha^2\left[\frac{J^2 - m_J^2}{2J(2J-1)(2J+1)} - \frac{(J+1)^2 - m_J^2}{2(J+1)(2J+1)(2J+3)}\right]$$

$$- eq_1Q_1\frac{[3m_J^2 - J(J+1)][3m_1^2 - I_1(I_1+1)]}{4I_1(2I_1-1)(2J-1)(2J+3)} + c_1m_1m_J + c_2m_2m_J + \frac{2g_1g_2\mu_N^2}{r^3(2J+3)(2J-1)}m_1m_J[3m_J^2 - J(J+1)].$$

(b) For $|m_J| = 1$ and $|m_J + m_1| < I_1$ there are two energy values:

$$W_\pm = \frac{\hbar^2}{2A}J(J+1) + \frac{\hbar^2}{2A}\alpha^2\left[\frac{J^2 - 1}{2J(2J-1)(2J+1)} - \frac{(J+1)^2 - 1}{2(J+1)(2J+1)(2J+3)}\right]$$

$$- eq_1Q_1\frac{[3 - J(J+1)]\{[3m_1^2 + 6m_1 + 6] - I_1(I_1+1)\}}{4I_1(2I_1-1)(2J-1)(2J+3)} - c_1 - \frac{2g_1g_2\mu_N^2[3 - J(J+1)]}{r^3(2J+3)(2J-1)}$$

$$\pm \left\{\left[\frac{eq_1Q_1[3 - J(J+1)]}{4I_1(2I_1-1)(2J-1)(2J+3)}(6m_1+6) + c_1(m_1+1) + c_2m_2 + \frac{2g_1g_2\mu_N^2(m_1+1)}{r^3(2J-1)(2J+3)}[3 - J(J+1)]\right]^2\right.$$

$$\left. + \left[\frac{3eq_1Q_1}{8I_1(2I_1-1)(2J-1)(2J+3)}\right]^2[(J+1)^2J^2(I_1-m_1)(I_1-m_1-1)(I_1+m_1+1)(I_1+m_1+2)]\right\}^{\frac{1}{2}}.$$

The zeroth order eigenfunctions for case (a) are characterized by the quantum numbers $(J, I_1, I_2, m_J, m_1, m_2)$ and will be denoted $\phi(J, I_1, I_2, m_J, m_1, m_2)$. The two eigenfunctions for case (b) have the quantum numbers $(J, I_1, I_2, |m_J| = 1, m_1, m_2)$ and will be linear combinations of the two states $\phi(J, I_1, I_2, 1, m_1, m_2)$ and $(J, I_1, I_2, -1, m_1+2, m_2)$. The correct linear combination can be chosen by the standard method of perturbation theory applied to two degenerate states.

The approximations involved in these results are (1) computation of the field energy to order α^2, (2) neglect of off-diagonal elements of the quadrupole operator which connect states with different field energy, (3) neglect of off-diagonal elements of all the other internal interactions which connect states with different field energies or different quadrupole energies.

III. SELECTION RULES

In the electric resonance experiments transitions are induced by an applied radiofrequency field between different stationary states of the molecules in a static electric field. We shall only be concerned with transitions which do not involve changes in the rotational energy, $\hbar^2J(J+1)/2A$.

Selection rules will be given by considering the matrix elements of the part of the Hamiltonian associated with the radiofrequency field between the initial and final states: $H' = -\mathbf{\mu} \cdot \mathbf{E}'e^{-i\omega t}$. In practice $\mathbf{E}'$ has its largest components in directions perpendicular to that of the static field $\mathbf{E}$ (z-direction), but there may also be an appreciable component in the z-direction as well.

We notice first that there can be no non-vanishing matrix elements between two states which are eigenstates of $\mathbf{J}^2$ with the same eigenvalue. This can be

proved by expanding $\cos(\mathbf{\mu}, \mathbf{E}')$ with the aid of the addition theorem of spherical harmonics into terms involving either the factor $\cos\theta$ or $\sin\theta$ in which θ is the spherical coordinate angle between $\mathbf{\mu}$ and the z-axis. Such an expansion is possible provided the state is an eigenstate of $\mathbf{J}^2$. Since $\cos\theta$ and $\sin\theta$ have matrix elements[14] only when $\Delta J = \pm 1$, the theorem is proved.

The transitions induced in the experiments occur because the static electric field perturbs a state which in the absence of the field would have a single J value, and thereby mixes in rotational states $J+1$ and $J-1$ in a first-order perturbation. There can be non-vanishing matrix elements of $-\mathbf{\mu} \cdot \mathbf{E}'$ between the perturbed part of a state whose zeroth order eigenfunction is characterized by a quantum number J and the zeroth order part of a final state which is also characterized by the value J. Another way of expressing this is to say that we have dipole radiation which occurs because of the dipole moment induced by the action of the static electric field on the molecule. We now consider in detail the selection rules which apply to the various field conditions treated in Section II.

(A) Very Weak Field

The zeroth order eigenfunctions are $\phi(J, I_1, F_1, I_2, F, M)$ and the $-\mathbf{\mu} \cdot \mathbf{E}$ interaction adds a perturbed first order state. But $-\mathbf{\mu} \cdot \mathbf{E} = -\mu_z E$ and μ_z is the z-component of a vector of the type $\mathbf{P}$ treated by Condon and Shortley.[15] This follows from the facts that $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_2$, and $\mathbf{\mu}$ commutes with $\mathbf{I}_2$ and satisfies a certain commutation relation with respect to $\mathbf{F}$. Thus $-\mathbf{\mu} \cdot \mathbf{E}$ has

[14] E. U. Condon and G. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 53.

[15] Reference 14, p. 67. The proof that $\mathbf{\mu}$ is a $\mathbf{P}$ vector is given.

non-vanishing matrix elements only when $\Delta F = 0$, ± 1, $\Delta M = 0$, and $\Delta F_1 = 0$, ± 1. The discussion of the previous paragraph made clear that $\Delta J = \pm 1$.

The components of the part of the Hamiltonian

$$H' = -\mathbf{\mu} \cdot \mathbf{E}' e^{-i\omega t}$$

are again those of a $\mathbf{P}$ vector. Hence non-vanishing matrix elements of H' exist only when $\Delta F = 0$, ± 1, $\Delta F_1 = 0$, ± 1. Furthermore, for the term with μ_z, $\Delta M = 0$ and for those with μ_x or μ_y, $\Delta M = \pm 1$.

Thus from the results of the last two paragraphs we conclude that H' can induce a transition from a state with zeroth order eigenfunction $\phi(J, I_1, F_1, I_2, F, M)$ to another state with zeroth order eigenfunction $\phi(J, I_1, F_1', I_2, F', M')$ provided $\Delta F = 0$, ± 1, ± 2 and $\Delta F_1 = 0$, ± 1, ± 2. For a radiofrequency field parallel to the static field $\Delta M = 0$ and for a radiofrequency field perpendicular to the static field $\Delta M = \pm 1$.

(B) Weak Field

The zeroth order eigenfunctions for the weak field case are:

$\phi^0(J, I_1, F_1, m_{F_1}, I_2, m_2)$ for $M = m_{F_1} + m_2 \neq 0$ (case (a))

$$\begin{cases} [\phi^0(J, I_1, F_1, \tfrac{1}{2}, I_2, -\tfrac{1}{2}) + \phi^0(J, I_1, F_1, -\tfrac{1}{2}, I_2, +\tfrac{1}{2})]/\sqrt{2} \\ \text{or} \qquad\qquad\qquad\qquad\qquad\qquad \text{for} \quad M = 0 \quad \text{(case (b))} \\ [\phi^0(J, I_1, F_1, \tfrac{1}{2}, I_2, -\tfrac{1}{2}) - \phi^0(J, I_1, F_1, -\tfrac{1}{2}, I_2, +\tfrac{1}{2})]/\sqrt{2}. \end{cases}$$

Neither $-\mathbf{\mu} \cdot \mathbf{E}$ nor $-\mathbf{\mu} \cdot \mathbf{E} e^{-i\omega t}$ have matrix elements except for $\Delta m_2 = 0$. By an application of reasoning similar to that used for the "very weak" field case it follows that H' can induce a transition between two zeroth order eigenfunctions with the same J value provided $\Delta F_1 = 0$, ± 1, ± 2. For the z-component of $\mathbf{E}'$, $\Delta M = 0$ and for case (a) states $\Delta m_{F_1} = 0$, $\Delta m_2 = 0$, in addition. For the x or y components of $\mathbf{E}'$, $\Delta M = \pm 1$, and a transition in which the initial and final states are case (a) states has, in addition, $\Delta m_{F_1} = \pm 1$, $\Delta m_2 = 0$.

(C) Strong Field

The zeroth order eigenfunctions are:

$\phi^0(J, m_J, I_1, m_1, I_2, m_2)$ for $|m_J| \neq 1$ or $|m_J| = 1$

and

$$|m_J + m_1| = I_1 \quad \text{or} \quad I_1 + 1 \quad \text{case (a)}$$

$$\begin{cases} a_1 \phi^0(J, 1, I_1, m_1, I_2, m_2) + a_2 \phi^0(J, -1, I_1, m_1 + 2, I_2, m_2) \\ \qquad = \psi_I \quad \text{for} \quad |m_J| = 1, \quad |m_J + m_1| < I_1 \\ b_1 \phi^0(J, 1, I_1, m_1, I_2, m_2) + b_2 \phi^0(J, -1, I_1, m_1 + 2, I_2, m_2) \\ \qquad\qquad\qquad\qquad\qquad = \psi_{II} \quad \text{case (b)}. \end{cases}$$

The interaction with the static electric field will contribute a first-order perturbed eigenfunction:

$$\phi^{(1)} = \sum_{J'=J\pm1} \frac{[\phi^{(0)}(J', m_J, I_1, m_1, I_2, m_2) | -\mathbf{\mu} \cdot \mathbf{E} | \phi^{(0)}(J, m_J, I_1, m_1, I_2, m_2)]}{W_{J, m_J, I_1, m_1, I_2, m_2} - W_{J', m_J, I_1, m_1, I_2, m_2}} \phi^{(0)}(J', m_J, I_1, m_1, I_2, m_2) \text{ case (a)}.$$

There is a similar expression for the case (b) states. The added states for either unperturbed state are of the form of ψ_I and ψ_{II} but with $J \pm 1$ substituted for J. This is seen to be true because $-\mathbf{\mu} \cdot \mathbf{E}$ has non-vanishing matrix elements only between wave functions with the same values of the quantum numbers $(m_J, I_1, m_1, I_2, m_2)$ and $J' = J \pm 1$. Thus H' can induce transitions between states with the same value of J provided $\Delta m_2 = 0$. For the z-component of $\mathbf{E}'$, $\Delta(m_J + m_1) = 0$. In addition, for case (a) states $\Delta m_J = \pm 1$, $\Delta m_1 = 0$ and thus the initial and final states are identical. For the x and y components of $\mathbf{E}'$, $\Delta(m_J + m_1) = \pm 1$, and, in addition, for case (a) states $\Delta m_J = \pm 1$, $\Delta m_1 = 0$.

It should be remarked that the selection rules derived in this section apply only in the approximation to which the perturbation theory has been carried. A breakdown of these selection rules will appear if a higher order of perturbation theory is applied.

IV. LINE INTENSITIES

The problem of the line intensities in molecular beam electric resonance experiments is made difficult by certain features of the experimental arrangement. These features will be discussed later in this section.

(A) Observability Criterion

We now consider the so-called observability criterion, i.e., whether or not a transition which is allowed by the selection rules will actually be observed. In order to be observed a transition must be induced in the C-field which will result in a different deflection of the molecule in the B-field than would occur in the absence of the transition. If there is an adiabatic correspondence between the state of a molecule in the C-field and its state in the B-field, the transition in order that it shall be observed must be induced between two states in the B-field with different values of $|m_J|$, because the deflection of the molecule in the B-field depends on $|m_J|$.

We now develop rules to establish the adiabatic correspondence between states under C-field conditions and under B-field conditions. Usually in practice the static electric field intensity in the C-field region is much smaller than that in the B-field region and different sets of quantum numbers are required to specify states in the two cases. We consider a three vector system (I_1, I_2, J) in the absence of an electric field. A stationary state is characterized by an eigenvalue of the total angular momentum $\mathbf{F}$ and of the

component, M, of the total angular momentum in an arbitrary direction. Consider now that an electric field of any magnitude is applied in an adiabatic fashion. The total angular momentum $\mathbf{F}$ need no longer be a good quantum number but the component, M, in the field direction is a constant of the motion. Two rules suffice to establish the correspondence between a state at zero field and at an arbitrary field: (1) The M value is the same. (2) In the adiabatic transition from the zero field states to the arbitrary field states two states with like M values never coincide in energy.

An outline of proofs of these two rules will now be given. That the component of the total angular momentum in the direction of the applied field remains constant under adiabatic change of the field value follows immediately from the fact that this quantity is a good quantum number independent of the field value.

That states with the same M value do not coincide in energy at any field value is a special case of the following general theorem.[16] Consider a Hermitian matrix (H_{jk}) whose n^2 complex quantities depend on certain real parameters $\lambda_1, \lambda_2 \cdots$. For a certain set of values of the parameters we assume that the matrix is general, i.e., no relationship exists between the H_{jk} which does not follow from the Hermitian character of the matrix. In particular, then, for this set of values of the parameters the eigenvalues of the matrix are distinct. The theorem states that three λ-values must be changed in order to achieve coincidence of two eigenvalues of (H_{jk}). If (H_{jk}) is a real Hermitian matrix then it is sufficient to change two λ-parameters in order to bring two eigenvalues into coincidence.

The matrix elements of the Hamiltonian (1) constitute a real Hermitian matrix whose elements we regard as functions of the field parameter, $\mathbf{E}$. The component, M, of the total angular momentum in the direction of the applied electric field is a good quantum number; i.e., there are no matrix elements of the Hamiltonian connecting eigenstates with different M values. Hence, by the proper choice of representation, the matrix for the Hamiltonian can be split into submatrices which refer to different M values. If the eigenvalues of any one of these submatrices are distinct at zero field, the general theorem stated above assures that the eigenvalues will not coincide for any value of the electric field. In the special cases of interest to us we show that the eigenvalues referring to a given M value are indeed distinct at zero field.

A number of examples of the application of the observability criterion are to be found in the paper on[1] $K^{39}F$ and[2] RbF. It should be emphasized that the observability criterion that we have taken assumes that there are no non-adiabatic transitions induced as the molecule passes from the C-field to the B-field. The effective frequencies that a molecule sees as it passes from the C-field to the B-field are believed to be of the

order of several hundred kc/sec. Such frequencies are small compared to the transition frequencies observed, so non-adiabatic transitions of the type of the transitions observed are not expected. It is possible, however, that lower frequency non-adiabatic transitions do occur. These involve essentially a reorientation of the molecular system with respect to the field direction.[17] The refocusing of a $(1, \pm1)_A - (1, 0)_B$ beam[1] proves that non-adiabatic transitions occur somewhere in the region between the A- and B-fields. It is probable that these non-adiabatic transitions occur between the A- and C-fields because, owing to the presence of the collimator slit, the electric field conditions may be highly variable in this inter-field region. Non-adiabatic transitions between the A- and C-fields will influence the distribution of states present in the C-field and hence are important in determining what transitions will be seen.

(B) Relative Line Intensities

The line intensity problem in these experiments is complicated by the following features of the experimental arrangement.

(1) The distribution of the molecules of interest among the various states that they can have in the C-field region is not known. By molecules of interest is meant molecules which have passed through the A-field in a certain state of space quantization which depends on the refocusing conditions being employed. Only for such molecules can a transition induced in the C-field be observed. The distribution of these molecules among the states that they can have in the C-field region is not known because the exact character of the non-adiabatic transitions that occur in the interfield region between the A- and C-fields is not known. Relative line intensities will depend on the exact distribution of these molecules.

(2) The intensity of the radiofrequency field is adjusted to be high so that the maximum intensity of transition is observed. Hence the transition probability cannot be taken as simply proportional to the square of the product of a matrix element by the radiofrequency field intensity. It depends rather in the simple two state case upon a sin^2-function of these two quantities.[18] Relative line intensities will then depend upon the intensity of the radiofrequency field. But the exact value of the field is not known and cannot be determined easily.

V. HALF-FREQUENCY TRANSITIONS

Conditions are sometimes encountered experimentally in which the amplitude of the radiofrequency field is high compared with that of the static field. In this case we must consider the field free state as perturbed primarily by the radiofrequency field, and the transition, also induced by the radiofrequency field, is from the perturbed part of the initial state to the unperturbed

[16] J. Von Neumann and E. Wigner, Physik. Zeits. 30, 467 (1929).

[17] E. Majorana, Nuovo Cimento 9, (1932).
[18] H. C. Torrey, Phys. Rev. 59, 293 (1941).

part of the final state. It will be shown that in this circumstance a transition between two states m and n can be induced at a frequency of $(E_m - E_n)/2h$. Such a half-frequency transition can be regarded as a transition in which two quanta supply the energy for the transition.

We consider the time dependent perturbation of a state $\phi(J, I_1, F_1, I_2, F, M)$ by the radiofrequency field $\mathbf{E}'e^{-i\omega t}$ in the absence of a static field. M is the component of $\mathbf{F}$ in the direction of the z-axis, which is the direction in which the static field is normally applied. We use formulas (240$_1$) and (240$_2$) of Pauli's *Handbuch* article.[19] The initial states (n) will be $\phi_n^{(0)}(J, I_1, F_1, I_2, F, M)$. The energy does not depend on M, since no static field is to be present, but such a function is a suitable zeroth order eigenfunction for the perturbation calculation. The final states (m) will be $\phi_m^{(0)}(J, I_1, F_1'', I_2, F'', M'')$ in which J is the same as for the initial state.

$$\Omega'_{kl} = [k \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l] e^{-i\omega t} \exp\left[\frac{i}{\hbar}(E_k^0 - E_l^0)t\right]$$

is our perturbing matrix element

$$a_m^{(1)}(t) = -\frac{i}{\hbar}\sum_n a_{n(0)}^{(0)} \int_0^t \Omega'_{mn}(t)dt$$

in which the a's are state amplitudes and the superscripts refer to the order of perturbation.

This first-order perturbation yields a zero result since there are no matrix elements of Ω' between states with the same J. Second-order perturbation theory yields:

$$a_m^{(2)}(t) = -\frac{1}{\hbar^2}\sum_n a_{n(0)}^{(0)} \sum_l \int_0^t \Omega'_{ml}(\tau)d\tau \int_0^\tau \Omega'_{l,n}(\tau')d\tau'$$

$$= -\frac{1}{\hbar^2}\sum_n a_{n(0)}^{(0)} \sum_l [m \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l][l \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, n]$$

$$\times \left\{ \int_0^t e^{-i\omega\tau} \exp\left[\frac{i}{\hbar}(E_m^{(0)} - E_l^{(0)})\tau\right]d\tau \right.$$

$$\left. \times \int_0^\tau e^{-i\omega\tau'} \exp\left[\frac{i}{\hbar}(E_l^{(0)} - E_n^{(0)})\tau'\right]d\tau' \right\}.$$

Evaluation of the bracketed expression yields:

$$\{\ \} = \frac{\exp\left[-i2\omega t + \frac{i}{\hbar}(E_m^{(0)} - E_n^{(0)})t\right] - 1}{\left[-i\omega + \frac{i}{\hbar}(E_l^{(0)} - E_n^{(0)})\right]\left[-2\omega i + \frac{i}{\hbar}(E_m^{(0)} - E_n^{(0)})\right]}$$

$$\frac{\exp\left[-i\omega t + \frac{i}{\hbar}(E_m^{(0)} - E_l^{(0)})t\right]}{\left[-i\omega + \frac{i}{\hbar}(E_l^{(0)} - E_n^{(0)})\right]\left[-i\omega + \frac{i}{\hbar}(E_m^{(0)} - E_l^{(0)})\right]}.$$

[19] W. Pauli, *Handbuch der Physik* (J. Springer, Berlin, 1933), second edition, Vol. 24/1.

The l states are all intermediate states which differ in rotational energy from the m and n states (the latter two states differ in quadrupole energy). Hence

$$\omega \ll \frac{E_l^{(0)} - E_n^{(0)}}{\hbar} \quad \text{or} \quad \frac{E_n^{(0)} - E_l^{(0)}}{\hbar}.$$

There can be no resonance for the second term at the frequencies we employ so it can be neglected. However, resonance can occur for the first expression which becomes:

$$\frac{\exp\left[-i2\omega t + i/\hbar(E_m^{(0)} - E_n^{(0)})t\right] - 1}{i/\hbar(E_l^{(0)} - E_n^{(0)})\left[-2\omega i + i/\hbar(E_m^{(0)} - E_n^{(0)})\right]}.$$

Our entire expression then becomes

$$a_m^{(2)}(t) = \frac{1}{\hbar^2}\sum_n a_{n(0)}^{(0)} \sum_l \frac{(m \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l)(l \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, n)}{[(E_l^{(0)} - E_n^{(0)})/\hbar]}$$

$$\times \frac{\exp\left[-i2\omega t + i/\hbar(E_m^{(0)} - E_n^{(0)})t\right] - 1}{[-2\omega + (E_m^{(0)} - E_n^{(0)}/\hbar)]}.$$

Normally we have a well-defined initial state, so there is no sum over n, and we get

$$a_m^{(2)} = \frac{1}{\hbar^2}a_{n(0)}^{(0)} \sum_l \frac{(m \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l)(l \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, n)}{[(E_l^{(0)} - E_n^{(0)})/\hbar]}$$

$$\times \frac{\exp\left[-i2\omega t + i/\hbar(E_m^{(0)} - E_n^{(0)})t\right] - 1}{[-2\omega + (E_m^{(0)} - E_n^{(0)})/\hbar]}.$$

Resonance occurs at: $\omega = (E_m^{(0)} - E_n^{(0)})/2\hbar$. The expression for $a_m^{(2)}$ is of the same form as the corresponding one for the normal transition with the principal exception that 2ω appears instead of ω. For the normal transition the matrix element $(l \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, n)$ would be replaced by $(l \,|\, \mathbf{\mu} \cdot \mathbf{E} \,|\, n)$ in which $\mathbf{E}$ is the static field intensity.

The selection rules for these half-frequency transitions are given by the following considerations. Non-vanishing matrix elements $(m \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l)$ and $(l \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, n)$ exist when $\Delta J = \pm 1$, $\Delta F_1 = 0, \pm 1$, and $\Delta F = 0, \pm 1$. Furthermore, if $\mathbf{E}'$ is perpendicular to the z-axis $\Delta M = \pm 1$ and if $\mathbf{E}'$ is parallel to the z-axis $\Delta M = 0$ (see Section III). Thus over-all selection rules for transitions from a state n to a state m with the same eigenvalue of $\mathbf{J}^2$ are $\Delta F_1 = 0, \pm 1, \pm 2, \Delta F = 0, \pm 1, \pm 2$. If $\mathbf{E}'$ is perpendicular to the z-axis $\Delta M = 0, \pm 2$; if $\mathbf{E}'$ has a component parallel to the z-axis as well $\Delta M = 0, \pm 1, \pm 2$. It will be noted that these selection rules are the same as for the normal case except for the selection rule involving M. Hence in so far as the M selection rule does not affect the situation all transitions are possible at the half-frequency which are possible at the normal frequency.

A study of the sums

$$\sum_l \frac{(m \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l)(l \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, n)}{[(E_l^{(0)} - E_n^{(0)})/\hbar]} \quad \text{and} \quad \sum_l \frac{(m \,|\, \mathbf{\mu} \cdot \mathbf{E}' \,|\, l)(l \,|\, \mathbf{\mu} \cdot \mathbf{E} \,|\, n)}{[(E_l^{(0)} - E_n^{(0)})/\hbar]}$$

in which E is the static field intensity will give a measure of the transition probabilities for the half-frequency transitions ($E=0$) and for the normal transitions ($E \neq 0$, $\omega = (E_m - E_n)/\hbar$) respectively. It was found for the case of interest to us ($J=1$ in the initial and final states) that these sums are comparable provided E' and E are of the same magnitude. Hence, if a normal transition is observed when E' and E are equal, it is expected that a half-frequency transition will be observed with this same value of E' when $E=0$.

The theory of half-frequency transitions in the presence of a static field is easily worked out. The representation $\phi(J, I_1, F_1, I_2, F, M)$ is applicable provided the static field is sufficiently weak. The expression $a_m^{(2)}$ for the case of zero field is modified to read:

$$a_m^{(2)} = -\frac{1}{\hbar^2}\sum_n a_n^{(0)}\sum_l (m|\mathbf{u}\cdot\mathbf{E}'|l)(l|\mathbf{u}\cdot\mathbf{E}'|n)\{\ \}$$

in which

$$\{\ \} = \frac{\exp\left[-i2\omega t + \frac{i}{\hbar}(E_m^{(0)} - E_n^{(0)})t\right] - 1}{\left[-i2\omega + \frac{i}{\hbar}(E_m^{(0)} - E_n^{(0)})\right]\left[-i\omega + i\frac{E_l^{(0)} - E_n^{(0)}}{\hbar}\right]}$$

$$-\frac{\exp\left[-i\omega t + \frac{i}{\hbar}(E_m^{(0)} - E_l^{(0)})t\right] - 1}{\left[-i\omega + \frac{i}{\hbar}(E_m^{(0)} - E_l^{(0)})\right]\left[-i\omega + i\frac{E_l^{(0)} - E_n^{(0)}}{\hbar}\right]}.$$

There is now a sum over a number of states n because our initial state is no longer a pure state $\phi(J, I_1, F_1, I_2, F, M)$, but involves a mixture of such states due to the perturbing effect of the static electric field. If the initial state were $\phi(J, I_1, F_1, I_2, F, M)$ in the absence of a static field, it will involve the states $\phi(J', I_1, F_1', I_2, F', M)$ in which $J' = J\pm 1$, $F_1' = F_1$, $F_1\pm 1$; $F' = F$, $F\pm 1$. Resonance occurs when $\omega = (E_m^{(0)} - E_n^{(0)})/2\hbar$ caused by the first factor within the brackets exactly as for the case of zero static field; at this resonance the second factor in the brackets is negligibly small. There is, of course, a first-order $a_m^{(1)}$ in this case which leads to the normal transitions between two states which at zero field have the same J value.

If the static field is sufficiently large so that the interaction of the field with the dipole moment is larger than the internal molecular interactions involving I_2, then a weak field representation should be used. The resonance at the half-frequencies is predicted exactly as above. The transition probability is reduced somewhat, however, because the amplitude of that part of the initial state which is involved in the half-frequency transition $[\phi(J, I_1, F_1, I_2, F, M)]$ is reduced by the perturbation due to the static field.

If the static field is sufficiently large so that a strong field condition applies $[\mu^2 E^2/(\hbar^2/2A)\gg eq_1Q_1]$ and if the radiofrequency field is perpendicular to the static field, then the M selection rule becomes $\Delta m_2 = 0$, $\Delta m_1 = 0$, $\Delta m_J = 0$, ± 2. Such a transition would not be observed for a $J=1$ state molecule because the deflection of a molecule in the A and B fields depends only upon $|m_J|$.

Professor I. I. Rabi first pointed out to us the possibility of half-frequency transitions. Also we wish to thank him for many stimulating discussions.

Hyperfine Structure and Isotope Shift in Barium

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(Received March 22, 1950)

Spectroscopic hyperfine structure studies with separated isotopes of barium have definitely confirmed a nuclear spin $\frac{3}{2}$ for the odd isotopes Ba[135] and Ba[137]. The lines of the even isotopes show no structure. The isotope shift is linear among masses of the same parity, but there is a relatively great odd-even shift: Note the order 138, 136, 134, 137, 135 in BaI, and 138, 136, 137, 134, 135 in BaII. The relative positions of the components (centroids, for odd masses) of the resonance lines, in $10^{-3}\pm 0.7.10^{-3}$ cm^{-1} are

	138	137	136	135	134
BaI $6s^2\ ^1S_0 - 6s6p\ ^1P_1$	0	+5.2	+2.2	+7.4	+4.4
BaII $6s\ ^2S_{\frac{1}{2}} - 6p\ ^2P_{\frac{1}{2}}$	0	+6.0	+4.8	+11.1	+9.6
$6s\ ^2S_{\frac{1}{2}} - 6p\ ^2P_{\frac{3}{2}}$	0	+6.4	+5.4	+12.6	+10.8

I. INTRODUCTION

SINCE hyperfine structure in the barium spectrum was reported by McLennan and Allen,[1] several investigators have tried to use the structure they found in several lines to determine the nuclear spin of the odd isotopes Ba[135] and Ba[137]. From the data of Ritschl and Sawyer,[2] Schuler and Jones[3] found the nuclear spin to

[1] J. C. McLennan and E. J. Allen, Phil. Mag. 8, 515 (1929).
[2] R. Ritschl and R. A. Sawyer, Zeits. f. Physik 72, 36 (1931).
[3] H. Kallman and H. Schuler, Ergeb. d. exakt. Naturwiss. 11, 134 (1932).