

Interaction of the Vibrational and Electronic Motions in Some Simple Conjugated Hydrocarbons

I. Exact Calculation of the Intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}, {}^1B_{2u}$ Vibronic Transitions of Benzene

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(Z. Naturforschg. **13 a**, 311—335 [1958]; eingegangen am 9. September 1957)

Eine Formel für die Einwirkung der Schwingungsstörungen auf die nicht entarteten elektronischen Energieniveaus wird unter folgenden Voraussetzungen abgeleitet:

- a) Das Molekül mag durch die BORN–OPPENHEIMER-Annäherung genau dargestellt sein;
 - b) in Übereinstimmung mit a) liegen annähernde Lösungen der Elektronen- und Schwingungs-SCHRÖDINGER-Gleichungen für eine bestimmte molekulare Geometrie vor;
 - c) die elektronischen Wellenfunktionen von b) können zu benachbarten Geometrien analytisch fortgesetzt werden;
 - d) Glieder von höherer als der ersten Ordnung der Kernverschiebungen sind vernachlässigbar in der Potenzreihenentwicklung der HAMILTON-Funktion und der elektronischen Wellenfunktionen von b);
 - e) die Störungstheorie erster Ordnung ist für die Annäherung d) genügend.
- Die so abgeleitete Formel wird zur Berechnung der Intensität der $({}^1A_{1g} \rightarrow {}^1B_{1u}, {}^1B_{2u})$ -Übergänge von Benzol verwendet. Obgleich die vorausgesetzte Intensität der ${}^1A_{1g} \rightarrow ({}^1B_{1u}, {}^1B_{2u})$ -Übergänge in guter Übereinstimmung mit dem Versuch steht, ist festgestellt worden, daß das Verhältnis der Intensitäten der Schwingungsübergänge in dem ${}^1A_{1g} \rightarrow {}^1B_{2u}$ -Elektronenübergang nicht in Übereinstimmung mit dem Versuch ist. Die Ursache dieser Diskrepanz wird festgestellt und Verbesserungen des Berechnungsverfahrens werden vorgeschlagen.

As is well-known, the solution of the dynamical equations for a polyatomic molecule is at present impossible; the mathematical difficulties are too great. One is thus forced from the outset to employ some approximation scheme in order to obtain a mathematical description of a polyatomic system. The usual procedure is to separate the dynamical equations into three distinct parts: the rotational, the vibrational, and the electronic parts. This procedure involves the neglect of terms coupling the rotational, vibrational, and electronic motions of a molecule. When this neglect is valid one can write the wave functions describing the polyatomic molecule as a product of rotational, vibrational, and electronic wave functions. Upon performing such a separation one usually examines the conditions for its validity and then attempts to make corrections for the errors introduced by such an approximation scheme. We shall, in this paper, only be concerned with means of correcting for the neglect of interaction terms which connect the electronic and vibrational motions.

When the nuclei forming the framework of a polyatomic molecule are allowed to move, both the electronic energy and the electronic wave function, describing the charge distribution in the molecule, change. Also the symmetry of the molecule is, in

general, lowered. Now there exist two types of phenomena which are intimately related to such changes. These phenomena are the intensity of spectral transitions and the stability of molecular configurations. Of these two phenomena only the former will be here discussed, a discussion of the latter being deferred until a future date.

Even though the probability of the occurrence of a given spectral transition may be, on symmetry grounds, zero for the equilibrium position of the nuclei, it is not necessarily zero for positions of the nuclei displaced from equilibrium; the molecule no longer has its original symmetry for such positions. Hence, certain spectral transitions may occur weakly in electronic band systems due to vibrational-electronic (vibronic) interactions.

How do we calculate such changes in the symmetry of electronic wave functions which have, initially, a zero transition probability with respect to the ground electronic state? The answer to this question is easily given. We assume that the vibrational motions merely "scramble" the solutions for the non-vibrating molecule; this is analogous to the description of an anharmonic oscillation by a superposition of harmonic vibrations. Thus we take the correct electronic wave function to be a linear combination of the equilibrium solutions, suitably gene-



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ralized so as to depend explicitly on the nuclear coordinates, and substitute the resulting wave function into the dynamical equations of motion. This procedure allows one to determine the extent of "mixing" of the equilibrium solutions needed to form the correct electronic functions. If the resultant wave function contains terms which have, with respect to the ground electronic state, a non-zero transition probability, we will have that the formerly "forbidden" band system is now allowed due to vibronic interactions. This type of calculation is here carried out in a non-empirical fashion for benzene.

The benzene spectrum is known to consist predominately of three band systems occurring at approximately $56,500\text{ cm}^{-1}$ ($^1A_{1g} \rightarrow ^1E_{1u}$), $50,000\text{ cm}^{-1}$ ($^1A_{1g} \rightarrow ^1B_{1u}$) and $39,500\text{ cm}^{-1}$ ($^1A_{1g} \rightarrow ^1B_{2u}$); the appropriate spectroscopic notation for each of the band systems has been given in parenthesis. The intensity of these bands in terms of the oscillator strength, f , is 0.9, 0.1, and 0.002, respectively. Hence, it is the latter two band systems which are of the "forbidden" type.

The non-empirical intensity calculation reported in this paper, yields the intensity of the "forbidden" benzene bands as $f=0.26$ and $f=0.003$, respectively. Although the calculated value for the absolute intensity of the $39,500\text{ cm}^{-1}$ band is in good agreement with experiment, the relative intensity distribution among the observed vibrational sub-levels composing this band is found to be incorrectly given. The error in the computed relative vibrational intensity distribution of the $39,500\text{ cm}^{-1}$ band is traced to the use of approximate normal co-ordinates for the $^1B_{2u}$ electronic state and to the use of simplifying assumptions with regard to the evaluation of certain integrals. The error in the calculated intensity of the $50,000\text{ cm}^{-1}$ is found to be caused by the incipient breakdown of the perturbation formulae here employed.

Outline of the Calculation

We shall in this section endeavor to present a detailed outline of the calculations contained in this paper. It is hoped that this outline will enhance the clarity of the paper.

In this work we are concerned with the phenomena produced by the interactions of nuclear and

electronic motions in non-degenerate electronic states. We shall deal with such interactions in degenerate electronic states in a forthcoming publication.

In Section 1 we begin our investigation of vibronic perturbations of stationary electronic states with a critical discussion of the applicability of the usual SCHRÖDINGER perturbation theory. Upon demonstrating that it leads to computational difficulties we develop a modified perturbation theory suitable for handling vibronic interactions. It is found that the usual formulae for the expansion coefficients of a perturbed wave function are modified by the addition of a term arising from the displacement of the wave functions from their equilibrium positions.

Since we are interested in applying the general formulae developed in Section 1 to a non-empirical calculation of the $^1A_{1g} \rightarrow (^1B_{1u}, ^1B_{2u})$ transitions in benzene, we next follow the well-known GOEPPERT-MAYER and SKLAR technique for the construction of both the zero order wave functions and the electronic-nuclear interaction terms of the molecular HAMILTONIAN of benzene. This construction occupies Sections 2.1 and 2.2. In the latter section, using an analytical continuation of the GOEPPERT-MAYER and SKLAR electronic-nuclear potential, we explicitly construct the vibronic perturbation for the problem.

The necessary perturbation and "overlap" matrices are algebraically computed in Sections 2.3 and 2.4; the necessary matrix elements being expressed in terms of nuclear displacements in the latter section. The evaluation of the necessary integrals is relegated to Appendices I through IV.

The formulae of Section 1, from which one calculates spectral intensities, contain integrals of the above computed matrix elements over the vibrational wave functions. In order to perform these integrations one must express the nuclear displacements occurring in Section 2.4 in terms of the appropriate normal co-ordinates. This task is executed in Section 2.5; the results of the substitution of these normal co-ordinates into the matrix elements of Section 2.4 are summarized in Section 2.6.

Having obtained the quantities required for the application of the intensity formulae of Section 1.4, we proceed to compute the intensity of the benzene $^1A_{1g} \rightarrow (^1B_{1u}, ^1B_{2u})$ electronic transitions in Section 2.7. The critical evaluation of the calculation, in the light of existing experimental data, is relegated in Section 2.8.

1. General Theory of Vibronic Interactions: Intensity Formulae *

1.1 Nuclear Displacements and Electronic Motions

From many points of view the most interesting properties of molecules involve displacements of their nuclei. An essential step in the analysis of such effects is the expression of the electronic eigenfunctions in terms of the internuclear distances. In many cases, of which the treatment of reaction kinetics is perhaps the most important, this step involves formidable difficulties that only diligent computation may circumvent. As a result, it has most frequently been handled phenomenologically. In other cases, however, where the associated nuclear motions are of small amplitude, as for example during vibrations, or associated with weak forces such as VAN DER WAALS attractions, the problems are more tractable. The successful elucidation of the latter dispersion forces was accomplished using perturbation methods. In this paper we shall be more concerned with intramolecular properties and therefore with vibrations.

Our most immediate interest is concerned with the intensities of formally "forbidden" electronic transitions. The importance of further work in the latter context has been underlined recently^{1,2} by the discovery that many of the most common band systems in the spectra of aromatic molecules owe but little of their intensities to purely electronic dipole strengths.

Accordingly, we shall utilize a perturbation theory approach in which the first-order terms in an expansion of the electronic eigenfunctions as a power series in the nuclear displacements are required. Throughout our analysis we shall adopt the BORN-OPPENHEIMER approximation^{3,4}, seeking solutions of eigenvalue problem

$$\mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a) = E_K(\tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a), \quad (1.1-1)$$

where $\mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a)$ is the complete molecular HAMILTONIAN lacking only the terms involving spin interactions and the kinetic energy terms for the nuclei. The electronic co-ordinates are designated by \mathbf{r}_i and the nuclear displacements by $\tilde{\mathbf{s}}_a$ in equation (1).

The spin-dependent wave functions Ψ_K , having been determined in this manner, will then be used to compute transition probabilities from which spectral intensities follow immediately in the well-known manner.

1.2 Choice of Representation

As stated in the introductory section 1.1 we shall begin our calculations with the equation

$$\mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a) = E_K(\tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a), \quad (1.2-1)$$

where $\mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a)$ consists of the four terms

$$\begin{aligned} \mathcal{T}_e &= -\frac{\hbar^2}{2m} \sum_i \nabla_i^2, & \mathcal{V}_e(\mathbf{r}_i) &= \sum_i \sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \\ \mathcal{V}_{e-n}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) &= -\sum_i \sum_a \frac{Z_a e^2}{|\mathbf{r}_i - \tilde{\mathbf{s}}_a|}, & (1.2-2) \\ \mathcal{V}_n(\tilde{\mathbf{s}}_a) &= \sum_{a,b} \frac{Z_a Z_b e^2}{|\tilde{\mathbf{s}}_a - \tilde{\mathbf{s}}_b - \tilde{\mathbf{x}}_{ab}|}. \end{aligned}$$

In (2) we have designated the electronic charge as e , the atomic number of nucleus a as Z_a , and the equilibrium internuclear distances as $|\tilde{\mathbf{x}}_{ab}|$, the vector being directed from atom a to atom b . The nuclear displacements $\tilde{\mathbf{s}}_a$ are hence measured from the positions of minimum molecular energy. Ψ_K is therefore an electronic eigenfunction for the K^{th} state of the molecule in the nuclear configuration $(\tilde{\mathbf{s}}_a)$. Hence when the eigenvalue $E_K(\tilde{\mathbf{s}}_a)$ is plotted as a function of the $\tilde{\mathbf{s}}_a$, it represents the usual potential energy surface for the nuclear motions. In particular, for nuclear configurations corresponding to "stable equilibrium," we have $\nabla_{\tilde{\mathbf{s}}_a=0} E_K = 0$ and $\sum_{a,b} (\tilde{\mathbf{s}}_a \cdot \nabla_{\tilde{\mathbf{s}}_a=0}) (\tilde{\mathbf{s}}_b \cdot \nabla_{\tilde{\mathbf{s}}_b=0}) E_K > 0$.

Now although it may be practicable to determine $\Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a)$ with reasonable accuracy for a particular, generally highly symmetric nuclear configuration $\tilde{\mathbf{s}}_a$, it is most undesirable to go further and to calculate its values over a representative set of points in $\tilde{\mathbf{s}}$ -space. The difficulties associated with solving the eigenvalue problem at the point where $\tilde{\mathbf{s}}_a = 0$, ($a = 0, 1, 2, \dots$), are sufficiently great that we do not wish to encounter them again and again at each displaced configuration of interest. Accordingly

* This section is the result of the joint researches of Prof. W. E. MOFFITT and the author. The theory outlined herein has been referred to as LIEHR and MOFFITT, Z. Naturforschg. **13a**, in previous publications of the author.

¹ W. E. MOFFITT, J. Chem. Phys. **22**, 320 [1954].

² W. E. MOFFITT, J. Chem. Phys. **22**, 1820 [1954].

³ M. BORN and R. OPPENHEIMER, Ann. Phys., Lpz. **84**, 457 [1927].

⁴ A. D. LIEHR, Ann. Phys., Lpz. **1**, 221 [1957].

we shall suppose that $\Psi_K(\mathbf{r}_i, 0) = \Theta_k(\mathbf{r}_i)$ to be known and use perturbation theory to determine its values at neighboring points in \mathbf{s} -space. So far as the dictates of a particular problem will allow, the point $\mathbf{s} = 0$ is naturally chosen so as to exhibit the HAMILTONIAN in its highest symmetry.

Formally, the most straightforward procedure is to expand $\Psi_K(\mathbf{r}_i, \mathbf{s}_a)$ in terms of the orthonormal set of functions $\Theta_k(\mathbf{r}_i) = \Psi_K(\mathbf{r}_i, 0)$,

$$\Psi_K(\mathbf{r}_i, \mathbf{s}_a) = \sum_j \Theta_j(\mathbf{r}_i) C_{jK}(\mathbf{s}_a), \quad (1.2-3)$$

determining the coefficients $C_{jK}(\mathbf{s}_a)$ by familiar methods. The usefulness of this expansion of course depends on the rapidity of convergence, the expansion becoming worthless from a computational point of view if the number of terms needed in the summation becomes very large. Indeed, this representation affords the most immediate way in which to derive the symmetry rules governing the influence of nuclear displacement on electronic motions⁵. In general, it is not, however, a satisfactory expansion for purposes of computation, since it converges only slowly.

This is most easily seen by noting that, in the zeroth order [where the summation in (3) is replaced by its first term $j=k$], the representation (3) does not allow a set of nuclei to take their orbital electrons with them as they move. Hence, in general, a large number of terms in the series must be devoted to remedying this defect alone, before considering any more subtle changes in electronic structure that may accompany the motion. It is these latter terms representing the associated variations in atomic and valence coupling that are responsible for the most important features of our problem.

There is, fortunately, an alternative procedure which arises quite naturally from the methods generally adopted for the solution of the "unperturbed" problem:

$$\mathcal{H}(\mathbf{r}_i, 0) \Psi_K(\mathbf{r}_i, 0) = E_K(0) \Psi_K(\mathbf{r}_i, 0), \quad (1.2-4)$$

i. e.,

$$\mathcal{H}_0 \Theta_k(\mathbf{r}_i) = E_k^0 \Theta_k(\mathbf{r}_i).$$

(We have denoted the unperturbed energy levels by k and the perturbed by K .) This procedure is to "continue" the functions $\Theta_k(\mathbf{r}_i)$, generally constructed from atomic orbitals according to valence bond or antisymmetrized molecular orbital theory,

by inserting in them their explicit dependence on the nuclear configuration. For example, a $2p_z$ atomic orbital such as one uses in π -electron theory is extended in the following manner:

$$\begin{aligned} \Phi_a(\mathbf{r}_i) &= N(\mathbf{r}_i \cdot \mathbf{f}) \exp[-(\bar{Z}_a |\mathbf{r}_a| / 2a_0)] \rightarrow \Phi_a(\mathbf{r}_i, \mathbf{s}_a) \\ &= N(\mathbf{r}_i - \mathbf{s}_a) \cdot \mathbf{f} \exp[-(Z_a |\mathbf{r}_i - \mathbf{s}_a| / 2a_0)] \end{aligned} \quad (1.2-5)$$

which follows immediately from a simple vector diagram. In general, the set of functions so defined will be complete at each and every nuclear configuration \mathbf{s} , and is therefore a suitable basis for an expansion of $\Psi_K(\mathbf{r}_i, \mathbf{s}_a)$:

$$\Psi_K(\mathbf{r}_i, \mathbf{s}_a) = \sum_j \Theta_j(\mathbf{r}_i, \mathbf{s}_a) C_{jK}(\mathbf{s}_a). \quad (1.2-6)$$

Moreover, it has the advantage that as a nucleus moves so, already in the zeroth order, it takes its orbital electrons along, the $\Theta_j(\mathbf{r}_i, \mathbf{s}_a)$ being called zeroth order functions. We may anticipate that expansion (6) converges much more rapidly than the series (3) on this account.

It should be noticed that whereas the functions $\Theta_j(\mathbf{r}_i, \mathbf{s}_a)$ are orthonormal at the point $\mathbf{s} = 0$, they do not retain this property in displaced configurations. That is, in general the matrix, whose elements are

$$S_{jk}(\mathbf{s}_a) = \int \Theta_j^*(\mathbf{r}_i, \mathbf{s}_a) \Theta_k(\mathbf{r}_i, \mathbf{s}_a) d\tau(\mathbf{r}_i), \quad (1.2-7)$$

is identical with the unit matrix at the origin, $\mathbf{s} = 0$, alone. It would, of course, be possible to adopt some orthogonalization procedure but, although this may be desirable for certain purposes, we shall find it unnecessary to do so here.

1.3 Perturbation Theory

Let us therefore suppose we have satisfactorily solved the "unperturbed" problem (1.2-4) in terms of a particular molecular theory characterized by its choice of functions Θ_j and let the non-degenerate function Θ_k be the zeroth order function. It is now our aim to determine the first order energies and eigenfunctions.

Since the basic representation that we use is itself a function of these displacements, and therefore also of the perturbation which exemplifies these, the theory is somewhat different than usual. We shall denote by primes the first order changes in the wave functions and the HAMILTONIAN due to a nuclear displacement, i. e., terms linear in the nuclear co-ordinates.

⁵ G. HERZBERG and E. TELLER, Z. Phys. Chem. B **21**, 410 [1933].

Hence

$$\begin{aligned}\mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) &\approx \mathcal{H}_0(\mathbf{r}_i) + \sum_a \tilde{\mathbf{s}}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} \mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) = \mathcal{H}_0 + \mathcal{H}' \\ \Theta_j(\mathbf{r}_i, \tilde{\mathbf{s}}_a) &\approx \Theta_j(\mathbf{r}_i) + \sum_a \tilde{\mathbf{s}}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} \Theta_j(\mathbf{r}_i, \tilde{\mathbf{s}}_a) = \Theta_j^0 + \Theta_j', \\ C_{jK}(\tilde{\mathbf{s}}_a) &\approx C_{jK}(0) + \sum_a \tilde{\mathbf{s}}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} C_{jK}(\tilde{\mathbf{s}}_a) = \delta_{jk} + C'_{jK}.\end{aligned}\quad (1.3-1)$$

where $\delta_{jk} = 0$ if $(j \neq k)$, 1 if $(j = k)$ [since the "unperturbed" function is taken to be $\Theta_k^0(\mathbf{r}_i)$]. We assume here that the state of interest, namely K , is non degenerate. The discussion of the degenerate case will be resumed in other communications^{6,7}.

We now proceed to minimize the energy $E_K(\tilde{\mathbf{s}}_a)$ in (1.2-1) with respect to the $C_{jK}(\tilde{\mathbf{s}}_a)$, which characterize our trial function (1.2-6), keeping the nuclear co-ordinates $\tilde{\mathbf{s}}_a$ fixed (this is equivalent to a first order perturbation theory treatment, as may be readily verified). One thus obtains the following series of equations: Since

$$\mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a) = E_K(\tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a),$$

we have

$$E_K(\tilde{\mathbf{s}}_a) \int \Psi_K^*(\mathbf{r}_i, \tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a) d\tau_{\text{el.}} = \int \Psi_K^*(\mathbf{r}_i, \tilde{\mathbf{s}}_a) \mathcal{H}(\mathbf{r}_i, \tilde{\mathbf{s}}_a) \Psi_K(\mathbf{r}_i, \tilde{\mathbf{s}}_a) d\tau_{\text{el.}};$$

which on using (1.2-6) becomes

$$E_K(\tilde{\mathbf{s}}_a) \sum_{l,m} C_{lK}^*(\tilde{\mathbf{s}}_a) S_{lm}(\tilde{\mathbf{s}}_a) C_{mK}(\tilde{\mathbf{s}}_a) = \sum_{l,m} C_{lK}^*(\tilde{\mathbf{s}}_a) H_{lm}(\tilde{\mathbf{s}}_a) C_{mK}(\tilde{\mathbf{s}}_a):$$

setting $\partial E_K(\tilde{\mathbf{s}}_a) / \partial C_{lK}^*(\tilde{\mathbf{s}}_a) = 0$ yields the secular equations

$$\sum_m E_K(\tilde{\mathbf{s}}_a) S_{lm}(\tilde{\mathbf{s}}_a) C_{mK}(\tilde{\mathbf{s}}_a) = \sum_m H_{lm}(\tilde{\mathbf{s}}_a) C_{mK}(\tilde{\mathbf{s}}_a). \quad (1.3-2)$$

At this point we use the expansions given in (1) to simplify the complicated set of equations given by (2). We first note that to first order

$$S_{lm}(\tilde{\mathbf{s}}_a) = \int (\Theta_l^{0*} + \Theta_l') (\Theta_m^{0*} + \Theta_m') d\tau(\mathbf{r}_i),$$

or,

$$S_{lm}(\tilde{\mathbf{s}}_a) = \delta_{l,m} + (\Theta_l | \Theta_m)'; \quad (1.3-3)$$

and similarly

$$H_{lm}(\tilde{\mathbf{s}}_a) = E_m^0 \delta_{l,m} + (\Theta_l | \mathcal{H}_0 | \Theta_m)' + H'_{lm}. \quad (1.3-4)$$

Substituting (3) and (4) in (2) yields then

$$\sum_m (E_K^0 + E'_K) [\delta_{l,m} + (\Theta_l | \Theta_m)'] [\delta_{m,k} + C'_{mK}] = \sum_m [E_m^0 \delta_{l,m} + (\Theta_l | \mathcal{H}_0 | \Theta_m)' + H'_{lm}] [\delta_{m,k} + C'_{mK}]. \quad (1.3-5)$$

Expanding equation (5) keeping only terms of the first order in the nuclear displacements gives one that

$$(E_K^0 - E_l^0) C'_{lK} + E'_K \delta_{l,k} = H'_{lk} + (\Theta_l | \mathcal{H}_0 - E_K^0 | \Theta_k)', \quad (1.3-6)$$

which reduces finally to

$$C'_{lK} = - \frac{H'_{lk} - (\Theta_l | \mathcal{H}_0 - E_K^0 | \Theta_k)'}{E_l^0 - E_K^0}, \quad l \neq k; \quad E'_K = (\Theta_k | \mathcal{H} | \Theta_k)', \quad l = k. \quad (1.3-7)$$

The coefficient C'_{kK} is determined, as in the more straightforward perturbation theory, by the normalization conditions for the first order wave functions. Equation (7) can be rewritten with the use of (1) as (1.3-8):

⁶ W.E. MOFFITT and A.D. LIEHR, Phys. Rev. **106**, 1195 [1957].

⁷ A.D. LIEHR and W.E. MOFFITT, J. Chem. Phys. (to be published).

$$C'_{lK} = - \frac{\int \Theta_l^{0*} \left(\sum_a \vec{s}_a \cdot \vec{\nabla}_{\vec{s}_a=0} \mathcal{H} \right) \Theta_k^0 d\tau(\mathbf{r}_i) - \sum_a \vec{s}_a \cdot \vec{\nabla}_{\vec{s}_a=0} \left\{ \int \Theta_l^* (\mathcal{H}_0 - E_K^0) \Theta_k d\tau(\mathbf{r}_i) \right\}}{E_l^0 - E_K^0}, \quad (1.3-8)$$

$$\vec{\nabla}_{\vec{s}_a=0} E_K = \vec{\nabla}_{\vec{s}_a=0} \left\{ \int \Theta_k^* \mathcal{H}(\mathbf{r}_i, \vec{s}_a) \Theta_k(\mathbf{r}_i, \vec{s}_a) d\tau(\mathbf{r}_i) \right\}, \quad l = k \quad (1.3-9)$$

$$\Psi_K(\mathbf{r}_i, \vec{s}_a) = \Theta_k^0(\mathbf{r}_i) + \Theta_k' + \sum_j \Theta_j^0(\mathbf{r}_i) C'_{jK}(\vec{s}_a). \quad (1.3-10)$$

If our functions $\Theta_l^0(\mathbf{r}_i)$ are exact solutions of the electronic SCHRÖDINGER equation, equations (7), (8), and (9) may be further simplified to read:

$$C'_{lK} = - \frac{H'_{lk} - (E_l^0 - E_K^0)(\Theta_l^0 | \Theta_k')}{E_l^0 - E_K^0}, \quad l \neq k, \quad (1.3-11)$$

$$\vec{\nabla}_{\vec{s}_a=0} E_K = \int \Theta_k^{0*} (\vec{\nabla}_{\vec{s}_a=0} \mathcal{H}) \Theta_k^0 d\tau(\mathbf{r}_i), \quad l = k. \quad (1.3-12)$$

We see that, for this case, equation (9) reduces to the HELLMANN⁸-FEYNMAN⁹ theorem¹⁰. In general, however, the wave functions $\Theta_l^0(\mathbf{r}_i)$ are only approximate solutions of the electronic SCHRÖDINGER equation, and hence, it is equations (8) and (9) which are valid, rather than (11) and (12). As we have here taken the configuration ($\vec{s}_a=0$) to be the stable equilibrium nuclear configuration, the right hand side of equation (9) [or equation (12), if the $\Theta_l^0(\mathbf{r}_i)$ are the true electronic wave functions] must vanish.

It is important to realize that the matrix element H'_{lk} does not involve the electron repulsion terms since, by definition (1.2-2),

$$\vec{\nabla}_{\vec{s}_a=0} \mathcal{T}_e = \vec{\nabla}_{\vec{s}_a=0} \mathcal{V}_e = 0.$$

Also, since \mathcal{V}_n is, from (1.2-2), independent of the electronic co-ordinates we have

$$\begin{aligned} \int \Theta_l^0 \left(\sum_a \vec{s}_a \cdot \vec{\nabla}_{\vec{s}_a=0} \mathcal{V}_n \right) \Theta_k^0 d\tau(\mathbf{r}_i) \\ = \left(\sum_a \vec{s}_a \cdot \vec{\nabla}_{\vec{s}_a=0} \mathcal{V}_n \right) \delta_{l,k} = 0, \quad l \neq k. \end{aligned} \quad (1.3-13)$$

Thus one need only consider the terms \mathcal{V}_{e-n} of (1.2-2) when computing H'_{lk} .

If one had employed the representation given in equation (1.2-3), one would have obtained the

coefficients C'_{lk} in the form

$$C'_{lk} = - \frac{H'_{lk}}{E_l^0 - E_K^0}. \quad (1.3-14)$$

This differs from the analogous quantities given in (8) by a term involving the variation of the matrix element, $(\Theta_l | \mathcal{H}_0 - E_K^0 | \Theta_k)$. This term represents an analytical continuation to the displaced domains in \vec{s} -space of the eigenfunctions of the original configuration. Inasmuch as (10) will in general converge more rapidly than (1.2-3), the former usage is likely to be more useful, and is in fact the one we shall adopt¹¹.

1.4. Spectral Intensities

In the BORN-OPPENHEIMER approximation the complete eigenfunction for the molecule, excluding only its rotational and translational degrees of freedom, may be written in the form^{3, 4}

$$\Omega_{Kk}(\mathbf{r}_i, \vec{s}_a) = \Psi_K(\mathbf{r}_i, \vec{s}_a) N_k^K(\vec{s}_a), \quad (1.4-1)$$

where the eigenfunction for the k^{th} vibrational state (electronic state K) satisfies

$$\{T_n + E_K(\vec{s}_a)\} N_k^K(\vec{s}_a) = W_k^K N_k^K(\vec{s}_a), \quad (1.4-2)$$

W_k^K being the vibrational energy eigenvalue. When the motion is essentially harmonic—that is, terms of order higher than $|\vec{s}_a|^2$ in the displacements are negligible in $E_k(\vec{s}_a)$ —this equation is separable and has solutions of the form^{12, 13}

$$N_k^K(\vec{s}_a) = h_{k(1)}^K(Q_1) h_{k(2)}^K(Q_2) \dots h_{k(v)}^K(Q_v), \quad (1.4-3)$$

where the Q_μ are the normal co-ordinates for the harmonic potential $E_K(\vec{s}_a)$; the subscripts affixed

⁸ H. HELLMAN, Einführung in die Quantenchemie, Verlag Deuticke, Leipzig 1937, p. 285.

⁹ R. P. FEYNMAN, Phys. Rev. **56**, 340 [1939].

¹⁰ For a quantitative comparison of the accuracy of eqs. (9) and (12) see A. D. LIEHR, Trans. Faraday Soc. **53**, 1533 [1957].

¹¹ For a quantitative comparison of the accuracy of eqs. (8), (11), and (14), see A. D. LIEHR, Canad. J. Phys. **35**, 1123 [1957].

¹² E. B. WILSON, JR., J. C. DECUS and P. C. CROSS, Molecular Vibrations, McGraw-Hill, New York 1955.

¹³ G. HERZBERG, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand, New York 1945.

to the separate factors give the degrees of excitation $k(\mu)$ of the μ^{th} normal modes.

In order to evaluate the transition probabilities between vibronic states for electric dipole radiation, we need the corresponding representatives of the electric moment operator \mathfrak{M} . This consists of two terms, one corresponding to the electrons only, namely

$$\mathfrak{M}_e = e \sum_i \mathbf{r}_i, \quad (1.4-4)$$

and another referring to the nuclei,

$$\mathfrak{M}_n = -e \sum_a Z_a \mathbf{r}_a = -e \sum_a Z_a \mathbf{r}_a^0 - e \sum_a Z_a \mathbf{s}_a. \quad (1.4-5)$$

In (5) we use \mathbf{r}_a^0 to denote the position vector of the undisplaced nucleus a and $-e Z_a$ the corresponding effective charge at nucleus a . The dipole strength of the vibronic transition $K, k \rightarrow L, l$ is now

$$\begin{aligned} \mathfrak{M}_{Kk, Ll} = & \int \Theta_K^{0*} \mathfrak{M}_e \Theta_L^0 d\tau_{el} \int N_k^{K*} N_l^L d\tau_n + \sum_j \int \Theta_K^{0*} \mathfrak{M}_e \Theta_j^0 d\tau_{el} \int N_k^K C'_{jL} N_l^L d\tau_n \\ & + \int \left(\int \Theta_K^{0*} \mathfrak{M}_e \Theta_L^0 d\tau_{el} + \int \Theta_K^{0*} \mathfrak{M}_e \Theta_l^0 d\tau_{el} \right) N_k^{K*} N_l^L d\tau_n + \sum_I \int \Theta_I^{0*} \mathfrak{M}_e \Theta_L^0 d\tau_{el} \int N_k^K C'_{IK} N_l^L d\tau_n. \end{aligned} \quad (1.4-8)$$

We must keep in mind in evaluating the integrals in (8) that the arguments of N_l^L must be changed to refer to the arguments of N_k^K in performing the final integrations. For strong band systems, which are allowed in the first order, the first term predominates. However, when the integral $\int \Theta_K^{0*} \mathfrak{M}_e \Theta_L^0 d\tau_{el}$ vanishes by symmetry, the band system is weaker and said to be "forbidden". The remaining terms in (8) are then all important. There are apparently also many cases where this integral nearly vanishes accidentally and for these the latter terms again predominate^{1, 2, 15}. Once we have obtained the quantity $\mathfrak{M}_{Kk, Ll}$ we are able to calculate the relevant intensities by the formula¹⁶

$$f_{Kk \rightarrow Ll} = 1.085 \cdot 10^{11} \frac{|\mathfrak{M}_{Kk, Ll}|^2}{e^2} E_{Kk \rightarrow Ll} \text{ cm}^{-1}, \quad (1.4-9)$$

where $f_{Kk \rightarrow Ll}$ is the so-called oscillator strength of the transition $Kk \rightarrow Ll$. The total intensity of a given electronic band, $K \rightarrow L$ say, is then given by sum of the $f_{Kk \rightarrow Ll}$ for all allowed vibrational transitions $k \rightarrow l$.

given by the squared length of the vector

$$\mathfrak{M}_{Kk, Ll} = \int \int \Omega_{Kk}^* (\mathfrak{M}_e + \mathfrak{M}_n) \Omega_{Ll} d\tau_{el} d\tau_n. \quad (1.4-6)$$

In order to assess the intensity of absorption bands in electronic spectra, we need treat the case $K \neq L$, for which

$$\mathfrak{M}_{Kk, Ll} = \int \int \Psi_K^* \mathfrak{M}_e \Psi_L d\tau_{el} N_k^{K*} N_l^L d\tau_n, \quad (1.4-7)$$

since Ψ_K, Ψ_L are orthogonal for all values of \mathbf{s} (the case $K=L$ corresponds to infrared intensities and thus will not be considered in this paper)¹⁴. Using expression (1.3-10) for the (Ψ_K, Ψ_L) , in which we choose as our reference point the equilibrium configuration for the ground state—though this will not, of course, be the equilibrium configuration in the excited electronic state L , say—we obtain

2. Non-Empirical Calculation of the Intensity of the "Forbidden" ${}^1A_{1g} \rightarrow {}^1B_{1u}$ and ${}^1A_{1g} \rightarrow {}^1B_{2u}$ Transitions of Benzene

2.1. Construction of the Appropriate Wave Functions

Of the four valence electrons belonging to each carbon atom in benzene, three are in sp^2 hybridized orbitals, giving rise to the single bonds to neighboring carbon and hydrogen atoms, while the fourth is in a $2p\pi$ orbital. The angles between the three sp^2 hybridized wave functions at each atom determine the geometry of the benzene molecule. The electrons in the $2p\pi$ orbitals are regarded as being free to circulate around the benzene ring and are thus responsible for the aromatic properties of benzene. We shall here be concerned only with the different molecular states of the six electrons of benzene which are assigned to the $2p\pi$ orbitals, (Φ_r) .

Numbering the carbon atoms serially from 0 to 5, we take the z -axis perpendicular to the hexagonal benzene molecule, the y -axis passing through the carbon atom numbered zero and the x -axis bisecting

¹⁴ A discussion of infrared intensities is given in R. DAUDEL and S. BRATOŽ, *Cahier Phys.* **75**–**76**, 39 [1956], and in S. BRATOŽ, *C. R. Acad. Sci., Paris* **243**, 1493 [1956].

¹⁵ D. S. McCLURE, *J. Chem. Phys.* **22**, 1668 [1954].

¹⁶ R. S. MULLIKEN and C. A. RIEKE, *Rep. Prog. Phys.* **8**, 231 [1941].

the bond between carbon atoms 1 and 2. With this convention we may write the low lying benzene singlet state wave functions, Θ_s , ($s = N, u, v, x, y$), as¹⁷

$$\begin{aligned}\Theta_N &= (6!)^{-1/2} [\psi_0(1) \bar{\psi}_0(2) \psi_1(3) \bar{\psi}_1(4) \\ &\quad \cdot \psi_{-1}(5) \bar{\psi}_{-1}(6)], \\ \Theta_u &= \frac{1}{2} (\Theta_1 + \Theta_{-1} - \Theta_2 - \Theta_{-2}) \\ &= \Re \Theta_1 - \Re \Theta_2, \\ \Theta_v &= \frac{1}{2i} (\Theta_1 - \Theta_{-1} - \Theta_2 + \Theta_{-2}) \quad (2.1-1) \\ &= \Im \Theta_1 - \Im \Theta_2, \\ \Theta_x &= \frac{1}{2} (\Theta_3 + \Theta_{-3} - \Theta_4 - \Theta_{-4}) \\ &= \Re \Theta_3 - \Re \Theta_4, \\ \Theta_y &= \frac{1}{2i} (\Theta_3 - \Theta_{-3} - \Theta_4 + \Theta_{-4}) \\ &= \Im \Theta_3 - \Im \Theta_4,\end{aligned}$$

where

$$\begin{aligned}\psi_{\xi} &= \sigma_{\xi} \sum_{r=0}^5 (\omega^{\xi})^r \Phi_r, \quad \omega = \exp[2\pi i/6], \\ (\xi &= 0, \pm 1, \pm 2, 3),\end{aligned} \quad (2.1-2)$$

$$\begin{aligned}\sigma_{\xi} &= \left[6 \left(1 + 2s_{01} \cos \frac{\pi \xi}{3} \right. \right. \\ &\quad \left. \left. + 2s_{02} \cos \frac{2\pi \xi}{3} + s_{03} \cos \pi \xi \right) \right]^{-1/2},\end{aligned} \quad (2.1-3)$$

$$s_{rs} = \int \Phi_r \Phi_s d\tau_{\text{el}}, \quad (2.1-4)$$

$$\begin{aligned}\Theta_1 &= (6!)^{-1/2} [\psi_0(1) \bar{\psi}_0(2) \psi_1(3) \bar{\psi}_1(4) \\ &\quad \psi_{-1}(5) \bar{\psi}_2(6)] = \Theta_{-1}^*,\end{aligned} \quad (2.1-5)$$

$$\begin{aligned}\Theta_2 &= (6!)^{-1/2} [\psi_0(1) \bar{\psi}_0(2) \psi_1(3) \bar{\psi}_1(4) \\ &\quad \bar{\psi}_{-1}(5) \psi_2(6)] = \Theta_{-2}^*,\end{aligned} \quad (2.1-6)$$

$$\begin{aligned}\Theta_3 &= (6!)^{-1/2} [\psi_0(1) \bar{\psi}_0(2) \psi_1(3) \bar{\psi}_1(4) \\ &\quad \psi_{-1}(5) \bar{\psi}_{-2}(6)] = \Theta_{-3}^*,\end{aligned} \quad (2.1-7)$$

$$\begin{aligned}\Theta_4 &= (6!)^{-1/2} [\psi_0(1) \bar{\psi}_0(2) \psi_1(3) \bar{\psi}_1(4) \\ &\quad \bar{\psi}_{-1}(5) \psi_{-2}(6)] = \Theta_{-4}^*.\end{aligned} \quad (2.1-8)$$

It may be readily verified that the functions (Θ_x, Θ_u) belong to the irreducible representation E_{1u} and that the functions ($\Theta_N, \Theta_u, \Theta_v$) belong to the irreducible representations (A_{1g}, B_{1u}, B_{2u}), respectively. Hence, if we neglect configuration interaction, the functions Θ_s ($s = x, y, u, v, N$) are the required wave functions for the ${}^1E_{1u}$, ${}^1B_{1u}$, ${}^1B_{2u}$, and ${}^1A_{1g}$ states of benzene. Indeed, we shall, in the interests

of simplicity, employ this approximation in computing the intensity of the "forbidden" ${}^1A_{1g} \rightarrow {}^1B_{1u}$, ${}^1B_{2u}$ spectral transitions of benzene.

2.2. Determination of the Vibronic Perturbation for Benzene

In sections 1.3 and 4 we have seen that, among other things, one requires the quantity

$$\mathcal{H}' = \sum_a \tilde{s}_a \cdot \nabla_{\tilde{s}_a=0} \mathcal{H}$$

if one wishes to calculate the intensity of the "forbidden" spectral transitions of benzene. Hence, we shall now express the HAMILTONIAN of the benzene molecule in terms of the nuclear displacements and determine its first-order variation with respect to these displacements.

As was seen in section 1.3 one need only consider the term \mathcal{V}_{e-n} of (1.2-2) in calculating \mathcal{H}' . Since each term in the expression (1.2-2) for \mathcal{V}_{e-n} represents the attraction of a given carbon nucleus for a $2p\pi$ electron plus the repulsion of that $2p\pi$ electron by the other five electrons on the given carbon atom, the effective charge Z_a in \mathcal{V}_{e-n} is a function both of the distance $r_a(i)$ that the electron is from carbon atom a , and of the distance \tilde{s}_a that the carbon atom a has been displaced due to skeletal vibrations. We shall here follow the GOEPPERT-MAYER and SKLAR procedure¹⁷ for evaluating $Z_a[r_a(i), \tilde{s}_a]$.

In evaluating the potential

$$\mathcal{V}_{e-n}^{(a)} = -Z_a e^2 / |r_a(i) - \tilde{s}_a|,$$

the two electrons of the inner shell of the carbon atom shall be treated as if they were located in the nucleus. $\mathcal{V}_{e-n}^{(a)}(i)$ is then the electrostatic potential experienced by electron i due to a nucleus of charge four, plus the potential due to the three sp^2 electrons, one electron being located in each of the three $2sp\sigma$ hybridized wave functions. The calculation of the vibronic perturbation can be simplified by noticing that $\mathcal{V}_{e-n}^{(a)}$ is also the potential of a neutral carbon atom with one electron assigned to the $2s$ and each of the three $2p$ carbon wave functions, minus the potential of a $2p\pi$ electron.

The attraction of a neutral carbon atom, a , in the valence state sp^3 for an electron follows easily from classical electrostatics as:

¹⁷ M. GOEPPERT-MAYER and A. L. SKLAR, J. Chem. Phys. 6, 645 [1938].

$$\mathcal{V}_{e-n}^{(a)}(i) = -\frac{4e^2}{|\mathbf{r}_a'(i)|} + \frac{e^2}{|\mathbf{r}_a'(i)|} \int_0^{\mathbf{r}_a'(i)} \sigma(t) t^2 dt + \int_{\mathbf{r}_a'(i)}^{\infty} e^2 \sigma(t) t dt, \quad (2.2-1)$$

where $\sigma(t)$,

$$\sigma(t) = 4\pi \{|\Phi_{2s}|^2 + |\Phi_{p_x}|^2 + |\Phi_{p_y}|^2 + |\Phi_{p_z}|^2\}, \quad (2.2-2)$$

is the charge distribution of the four sp^3 electrons and $\mathbf{r}_a'(i)$ signifies the distance of the electron i

from the nucleus of carbon atom a . Thus $\int_0^{\infty} \sigma(t) t^2 dt$

must equal four. If we return to the notation of equation (1.2-2) where $\mathbf{r}_a(i)$ is the distance of electron i from the *equilibrium position* of carbon atom a and \mathbf{s}_a is the deviation of carbon atom a from that equilibrium position, we may write

$$\mathbf{r}_a'(i) = \mathbf{r}_a(i) - \mathbf{s}_a. \quad (2.2-3)$$

$$\begin{aligned} \mathcal{V}_{e-n}(\vec{Q}, \vec{s}) = & -\frac{Ze^2}{a_0} \sum_{a=0}^5 \left[\frac{1}{|\vec{Q}_a - \mathbf{s}_a|} + \frac{12P_2(\cos \vartheta_a)}{|\vec{Q}_a - \mathbf{s}_a|^3} + \frac{\exp(-|\vec{Q}_a - \mathbf{s}_a|)}{24|\vec{Q}_a - \mathbf{s}_a|} (5|\vec{Q}_a - \mathbf{s}_a|^3 + 18|\vec{Q}_a - \mathbf{s}_a|^2 \right. \\ & + 54|\vec{Q}_a - \mathbf{s}_a| + 72) - \frac{P_2(\cos \vartheta_a) \exp(-|\vec{Q}_a - \mathbf{s}_a|)}{12|\vec{Q}_a - \mathbf{s}_a|^3} \\ & \left. \cdot (|\vec{Q}_a - \mathbf{s}_a|^5 + 6|\vec{Q}_a - \mathbf{s}_a|^4 + 24|\vec{Q}_a - \mathbf{s}_a|^3 + 72|\vec{Q}_a - \mathbf{s}_a|^2 + 144|\vec{Q}_a - \mathbf{s}_a| + 144) \right], \end{aligned} \quad (2.2-6)$$

where ϑ_a is the angle between the z -axis and the vector $\vec{Q}_a - \mathbf{s}_a$ (that is, $\cos \vartheta_a = \mathbf{f} \cdot (\vec{Q}_a - \mathbf{s}_a) / |\vec{Q}_a - \mathbf{s}_a|$) and $P_l(\cos \vartheta_a)$ is the l^{th} order LEGENDRE polynomial.

We are now in a position to calculate the desired vibronic perturbation

$$\mathcal{H}' = \sum_a \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} \mathcal{H} = \sum_a \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} \mathcal{V}_{e-n}(\vec{Q}, \vec{s}). \quad (2.2-7)$$

Making use of the relations

$$\begin{aligned} \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} P_2(\cos \vartheta_a) &= \frac{3(\vec{Q}_a \cdot \mathbf{s}_a)}{Q_a^2} \cos^2 \vartheta_a \\ &\quad - \frac{3(\mathbf{s}_a \cdot \mathbf{f})}{Q_a} \cos \vartheta_a, \\ \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} e^{-\frac{Q_a - \mathbf{s}_a}{Q_a}} &= \frac{\vec{Q}_a \cdot \mathbf{s}_a}{Q_a} e^{-\frac{Q_a}{Q_a}}, \end{aligned} \quad (2.2-8)$$

$$\mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} |\vec{Q}_a - \mathbf{s}_a|^{-1} = -e(\vec{Q}_a \cdot \mathbf{s}_a) Q_a^{-2},$$

we obtain upon substitution of (6) into (7), the required result [neglecting terms containing

substitution of (3) into (1) yields the desired form of $\mathcal{V}_{e-n}^{(a)}(i)$.

To determine $\mathcal{V}_{e-n}^{(a)}(i)$ one must yet compute the potential of a $2p\pi$ electron,

$$-\int \frac{e^2}{|\mathbf{r}'(i) - \mathbf{t}(i)|} d\tau[\mathbf{t}(i)], \quad (2.2-4)$$

as well as evaluate the integrals occurring in (1). Letting

$$\vec{Q}_a(i) = \frac{Z\mathbf{r}_a(i)}{a_0} \quad \text{and} \quad \mathbf{s}_a = \frac{Z\mathbf{s}_a}{a_0},$$

where Z equals 3.18 and a_0 is the BOHR radius of hydrogen, we have¹⁷

$$\begin{aligned} \Phi_{2s} &= N_0(2 - \varrho) e^{-\varrho/2}, \quad N_0 = (Z^3/32\pi a_0^3)^{1/2}, \\ \Phi_{2p_x} &= N_0 \varrho e^{-\varrho/2} \sin \vartheta \cos \varphi, \\ \Phi_{2p_y} &= N_0 \varrho e^{-\varrho/2} \sin \vartheta \sin \varphi, \\ \Phi_{2p_z} &= \Phi_{2p\pi} = N_0 \varrho e^{-\varrho/2} \cos \vartheta. \end{aligned} \quad (2.2-5)$$

Substitution of (5) into (2), (1), and (4) then yields

$(\mathbf{s}_a \cdot \mathbf{f}) \cos \vartheta_a$ as a factor]:

$$\mathcal{H}'(i) = -\frac{Ze^2}{a_0} \sum_{a=0}^5 \frac{\vec{Q}_a \cdot \mathbf{s}_a}{Q_a} g_a(Q_a, \vartheta_a), \quad (2.2-9)$$

where

$$\begin{aligned} g_a(Q_a, \vartheta_a) &= \frac{1}{Q_a^2} - \frac{18}{Q_a^4} + \frac{90 \cos^2 \vartheta_a}{Q_a^4} + \frac{e^{-Q_a}}{4Q_a^4} [Q_a^6 + 2Q_a^5 \\ &\quad + 9Q_a^4 + 24Q_a^3 + 48Q_a^2 + 72Q_a + 72] - \frac{e^{-Q_a}}{8Q_a^4} \cos^2 \vartheta_a \\ &\quad \cdot [Q_a^6 + 6Q_a^5 + 30Q_a^4 + 120Q_a^3 + 360Q_a^2 + 720Q_a + 720]. \end{aligned} \quad (2.2-10)$$

The terms containing $(\mathbf{s}_a \cdot \mathbf{f}) \cos \vartheta_a$ as a factor were dropped from expression (9) since they lead to integrals over electronic co-ordinates which are zero by symmetry. This is easily seen from the fact that the product of all the π -electron wave functions occurring in any given integral is always even with respect to reflection in the plane of the benzene ring, whereas a perturbation term containing $\cos \vartheta_a$

linearly is of necessity odd, making the integral in question identically zero by symmetry. Hence the nuclear displacements perpendicular to the benzene ring cannot, to the first order, perturb the electronic wave functions which we are employing in the description of the benzene molecule.

2.3 The Perturbation and "Overlap" Matrices

We now wish to consider the calculation of the perturbation matrix (H'_{PT}) . ($P, T = x, y, u, v$), and the "overlap" matrix $[(P|\mathcal{H}_0 - E_T^0|T)']$ where

$$H'_{PT} = \int \Theta_P^{0*} \left(\sum_a \mathfrak{z}_a \cdot \nabla_{\mathbf{s}_a=0} \right) \Theta_T^0 d\tau_{\text{el.}} \quad (2.3-1)$$

$$\begin{aligned} (P|\mathcal{H}_0 - E_T^0|T)' \\ = \sum_a \mathfrak{z}_a \cdot \nabla_{\mathbf{s}_a=0} \left\{ \int \Theta_P^* [\mathcal{H}_0 - E_T^0] \Theta_T d\tau_{\text{el.}} \right\}, \end{aligned} \quad (2.3-2)$$

and so determine the extent of "scrambling" of the states Θ_T ($T = x, y, u, v$) under vibrational perturbations. Because of the complexity of the calculative procedures, we shall here only summarize the results of our computations.

To determine the form of the perturbation matrix we first turn to group theory. The normal vibrations for a ring of six carbon atoms (we neglect the "pure" hydrogen motions) belong to the species^{12, 13}

$$\Gamma_n = A_{1g} + B_{1u} + B_{2g} + B_{2u} + E_{1u} + 2E_{2g} + E_{2u}. \quad (2.3-3)$$

We thus see that since (Θ_x, Θ_y) are of species E_{1u} and (Θ_u, Θ_v) of species B_{1u} and B_{2u} , respectively, only the normal vibrations of symmetry E_{2g} may appear in the off-diagonal matrix elements H'_{PT} and $(P|\mathcal{H}_0 - E_T^0|T)'$, ($P \neq T = x, y, u, v$). Moreover, since the product wave function $\Theta_u \cdot \Theta_v$ is of symmetry species A_{2g} , the matrix elements H'_{PT} and $(P|\mathcal{H}_0 - E_T^0|T)'$, ($P \neq T = u, v$), are zero for all permissible skeletal carbon vibrations. Hence we have the results

$$\begin{aligned} H'_{PT} &= (P|\mathcal{H}_0 - E_T^0|T)' = 0, \quad (P \neq T = u, v) \\ H'_{PT} \text{ and } (P|\mathcal{H}_0 - E_T^0|T)' &\subset \Gamma_n(E_{2g}), \quad (P \neq T). \end{aligned} \quad (2.3-4)$$

We also have the configurational stability equation

$$H'_{PP} + (P|\mathcal{H}_0 - E_P^0|P)' = 0, \quad (2.3-5)$$

which follows from the fact that the benzene molecule is stable with respect to the nuclear displacements of symmetry A_{1g} which tend to destroy its hexagonal symmetry.

We now proceed to calculate the algebraic form of the matrix elements H'_{PT} . Utilizing definitions (2.1-2 and 3), one may readily verify that

$$\int \psi_{\xi}^{0*}(i) \mathcal{H}'(i) \psi_{\eta}^0(i) d\tau_{\text{el.}} = \sigma_{\xi} \sigma_{\eta} \sum_{r,s} \omega^{s\eta-r\xi} h'_{rs}, \quad (2.3-6)$$

where

$$h'_{rs} = \int \Phi_r^{0*}(i) \mathcal{H}'(i) \Phi_s^0(i) d\tau_{\text{el.}} \quad (2.3-7)$$

And by employing (6) and (7) one may then compute the integrals

$$H'_{ij} = \int \Theta_i^{0*} \mathcal{H}' \Theta_j^0 d\tau_{\text{el.}}, \quad (i, j = \pm 1, \pm 2, \pm 3, \pm 4), \quad (2.3-8)$$

which determine the perturbation matrix elements H'_{PT} ($P, T = x, y, u, v$). For example, we may now write

$$\begin{aligned} H'_{PP} &= H'_{33} = \kappa, \quad (P = x, y, u, v) \\ H'_{ux} &= \Re (H'_{13}^* + H'_{1-3}) = \Re \lambda, \\ H'_{vx} &= \Im (H'_{13}^* - H'_{1-3}) = \Im \mu, \quad (2.3-9) \\ H'_{uy} &= -\Im (H'_{13}^* + H'_{1-3}) = -\Im \lambda, \\ H'_{vy} &= \Re (H'_{13}^* - H'_{1-3}) = \Re \mu, \end{aligned}$$

where

$$\begin{aligned} \kappa &= \sum_{r,s} [2\sigma_0^2 + 3\sigma_1^2 \omega^{r-s} + \sigma_2^2 (\omega^2)^{r-s}] h'_{rs} \\ \lambda &= \sum_{r,s} [\sigma_2^2 (\omega^2)^{r+s} - \sigma_1^2 (\omega^{-1})^{r+s}] h'_{rs} \quad (2.3-10) \\ \mu &= \sum_{r,s} [\sigma_2^2 (\omega^2)^{r+s} + \sigma_1^2 (\omega^{-1})^{r+s}] h'_{rs}. \end{aligned}$$

The "overlap" matrix $(P|\mathcal{H}_0 - E_T^0|T)'$, ($P, T = u, v, x, y$), is obtained by methods analogous to those employed in the calculation of the benzene eigenfunctions, Θ_P^0 , and eigenvalues E_P^0 , ($P = N, u, v, x, y$). And as these methods are well-known^{17, 18} we shall here only summarize our results. Defining the quantities H'_{ij} , S'_{ij} , $(\zeta_{kl}^{ij})'$, and ε'_{ij} as

¹⁸ R. G. PARR, D. P. CRAIG and I. G. ROSS, J. Chem. Phys. **18**, 1561 [1950].

$$\begin{aligned}
H_{ij}^{0'} &= \sum_a \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} \left\{ \int \Theta_i^* \mathcal{H}_0 \Theta_j d\tau_{\text{el.}} \right\} & (i, j = \pm 1, \pm 2, \pm 3, \pm 4), \\
S_{ij}' &= \sum_a \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} \left\{ \int \psi_i^* \psi_j d\tau_{\text{el.}} \right\} & (i, j = 0, \pm 1, \pm 2, 3), \\
(\zeta_{kl}^{ij})' &= \sum_a \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} \left\{ \int \psi_i(1) \psi_j(1) \frac{e^2}{r_{12}} \psi_k(2) \psi_l(2) d\tau_1 d\tau_2 \right\}, \\
\varepsilon_{ij}' &= \sum_a \mathbf{s}_a \cdot \nabla_{\mathbf{s}_a=0} \left\{ \int \psi_i^*(1) [\mathcal{T}_e(1) + \mathcal{V}_{e-n}^0(1)] \psi_j(1) d\tau_1 \right\},
\end{aligned} \tag{2.3-11}$$

we may readily derive the results

$$\begin{aligned}
(x | \mathcal{H}_0 - E_u^0 | u)' &= \Re(\mathfrak{M} - E_u^0 \tilde{\mathfrak{M}}), & (y | \mathcal{H}_0 - E_u^0 | u)' &= \Im(\mathfrak{M} - E_u^0 \tilde{\mathfrak{M}}), \\
(x | \mathcal{H}_0 - E_v^0 | v)' &= \Im(\mathfrak{M} - E_v^0 \tilde{\mathfrak{M}}), & (y | \mathcal{H}_0 - E_v^0 | v)' &= \Re(\mathfrak{M} - E_v^0 \tilde{\mathfrak{M}}),
\end{aligned} \tag{2.3-12}$$

where

$$\begin{aligned}
\mathfrak{M} &= \frac{1}{2} (H_{31}^{0'} - H_{32}^{0'} + H_{3-1}^{0'} - H_{3-2}^{0'} - H_{41}^{0'} + H_{42}^{0'} - H_{4-1}^{0'} + H_{4-2}^{0'}), \\
\mathfrak{M} &= S'_{-22} (2\varepsilon_0^0 + 3\varepsilon_1^0 + \gamma_{00}^0 + 3\gamma_{11}^0 + 6\gamma_{01}^0 - 3\delta_{01}^0 - \delta_{1-1}^0) + \varepsilon'_{-22} - \varepsilon'_{1-1} \\
&\quad - S'_{1-1} (2\varepsilon_0^0 + 2\varepsilon_1^0 + \varepsilon_2^0 + \gamma_{00}^0 + \gamma_{11}^0 + 4\gamma_{01}^0 + 2\gamma_{02}^0 + 2\gamma_{12}^0 - 2\delta_{01}^0 - \delta_{02}^0 - \delta_{1-1}^0 - \xi^0 + \eta^0 + \delta_{1-2}^0 + \delta_{12}^0) \\
&\quad + (2\zeta_{22}^{00} - \zeta_{02}^{02} + 3\zeta_{22}^{1-1} - 2\zeta_{-1-1}^{00} - 2\zeta_{-1-1}^{1-1} - \zeta_{2-2}^{1-1} + \zeta_{0-1}^{0-1} + 2\zeta_{-1-2}^{1-2})',
\end{aligned} \tag{2.3-13}$$

$$\begin{aligned}
\mathfrak{M} &= \frac{1}{2} (H_{31}^{0'} - H_{32}^{0'} - H_{3-1}^{0'} + H_{3-2}^{0'} - H_{41}^{0'} + H_{42}^{0'} + H_{4-1}^{0'} - H_{4-2}^{0'}), \\
\mathfrak{M} &= S'_{-22} (2\varepsilon_0^0 + 3\varepsilon_1^0 + \gamma_{00}^0 + 3\gamma_{11}^0 + 6\gamma_{01}^0 - 3\delta_{01}^0 - \delta_{1-1}^0) + \varepsilon'_{-22} + \varepsilon'_{1-1} \\
&\quad + S'_{1-1} (2\varepsilon_0^0 + 2\varepsilon_1^0 + \varepsilon_2^0 + \gamma_{00}^0 + \gamma_{11}^0 + 4\gamma_{01}^0 + 2\gamma_{02}^0 + 2\gamma_{12}^0 - 2\delta_{01}^0 - \delta_{02}^0 - \delta_{1-1}^0 - \xi^0 - \eta^0 + \delta_{1-2}^0 + \delta_{12}^0) \\
&\quad + (2\zeta_{22}^{00} - \zeta_{02}^{02} + 3\zeta_{22}^{1-1} + 2\zeta_{-1-1}^{00} + 2\zeta_{-1-1}^{1-1} + \zeta_{2-2}^{1-1} - \zeta_{0-1}^{0-1} - 2\zeta_{-1-2}^{1-2})',
\end{aligned} \tag{2.3-14}$$

$$\tilde{\mathfrak{M}} = S'_{-22} - S'_{1-1}, \tag{2.3-15}$$

$$\tilde{\mathfrak{M}} = S'_{-22} + S'_{1-1}. \tag{2.3-16}$$

In equations (13) and (14) we have denoted the values of ε_{ij} and ζ_{kl}^{ij} at $\mathbf{s}=0$ by the notation^{17, 18} ε_i^0 and γ_{ij}^0 , δ_{ij}^0 , ξ^0 , and η^0 , respectively.

2.4 Calculation of the Matrix Elements

In computing the necessary matrix elements for the calculation of the intensity of the benzene spectral transitions ${}^1A_{1g} \rightarrow ({}^1B_{1u}, {}^1B_{2u})$, we shall express the nuclear displacement vector $\tilde{\mathbf{s}}$ in the WILSON type co-ordinates¹⁹ shown in Fig. 1. Since, as we have already noted in section 2.2, the integrand $\Phi_a(\vec{q}_a) \cos \vartheta_c \Phi_b(\vec{q}_b)$ is odd on reflection in the plane of the benzene ring (that is, under σ_h), all the

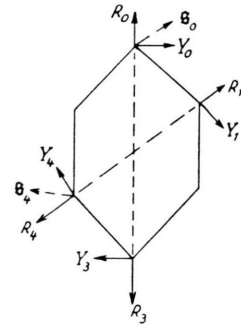


Fig. 1. Nuclear Displacement Co-ordinates for Benzene.

integrals, $\int \Phi_a \cos \vartheta_c f(q_c) \Phi_b d\tau_{\text{el.}}$, vanish identically. Thus we can forget about the z -component, $Z_a \vec{q}_a(i) \cos \vartheta_a(i)$, of the vibronic interactions, $\sum_a \vec{q}_a \cdot \tilde{\mathbf{s}}_a f(q_a)$, while calculating the matrix elements H'_{PT} and $(P | \mathcal{H}_0 - E_T^0 | T)'$, ($P, T = x, y, u, v$).

¹⁹ E. B. WILSON, JR., Phys. Rev. **45**, 706 [1934].

The detailed evaluation of the required matrix elements H'_{PT} and $(P|\mathcal{H}_0 - E_T^0|T)'$ is almost a separate topic in itself (see Appendices I through IV). Hence, we shall here only summarize the results of this evaluation. The substitution of eqs. (2.2–9 and 10) into eqs. (2.3–7 and 10) yields

$$\lambda = 6^{1/2} (a_\lambda \mathcal{R}_{-2} + i b_\lambda \mathcal{Y}_{-2}), \quad (2.4-1)$$

$$\mu = 6^{1/2} (a_\mu \mathcal{R}_{-2} + i b_\mu \mathcal{Y}_{-2}), \quad (2.4-2)$$

where we have defined \mathcal{R}_{-2} , \mathcal{Y}_{-2} , a_P and b_P , ($P = \lambda, \mu$), as

$$\mathcal{R}_{-2} = 6^{-1/2} \sum_r (\omega^{-2})^r R_r, \quad \omega = \exp[2\pi i/6], \quad (2.4-3)$$

$$\mathcal{Y}_{-2} = 6^{-1/2} \sum_r (\omega^{-2})^r Y_r, \quad (2.4-4)$$

$$a_P = [\sigma_2^2 - (-1)^P \sigma_1^2] \left[I_0(\bar{x}_{03}) - \cos \frac{\pi}{3} I_0(\bar{x}_{01}) - \sin \frac{\pi}{3} I_0(\bar{x}_{02}) \right] \quad (2.4-5)$$

$$+ 2[\sigma_2^2 + (-1)^P \sigma_1^2] \left[I_1(\bar{x}_{03}) - \cos \frac{\pi}{3} I_1(\bar{x}_{01}) - \cos \omega_3 s_{01} I_0\left(\sqrt{\frac{13}{4}} \bar{x}_{01}\right) + 2 \cos \omega_1 s_{01} I_0\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) - s_{03} I_0(\bar{x}_{01}) \right]$$

$$+ 2[\sigma_2^2 - (-1)^P \sigma_1^2] \left[s_{02} I_0\left(\frac{1}{2} \bar{x}_{01}\right) + s_{02} I_0\left(\frac{3}{2} \bar{x}_{01}\right) - \cos \omega_2 s_{02} I_0\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) - \sin \frac{\pi}{3} I_1(\bar{x}_{02}) \right],$$

$$b_P = 2 \sin \frac{\pi}{3} [\sigma_2^2 - (-1)^P \sigma_1^2] \left[\sin \frac{\pi}{3} I_0(\bar{x}_{01}) - \cos \frac{\pi}{3} I_0(\bar{x}_{02}) \right]$$

$$+ 4 \sin \frac{\pi}{3} [\sigma_2^2 + (-1)^P \sigma_1^2] \left[\sin \omega_3 s_{01} I_0\left(\sqrt{\frac{13}{4}} \bar{x}_{01}\right) - \sin \frac{\pi}{3} I_1(\bar{x}_{01}) \right] \quad (2.4-6)$$

$$+ 4 \sin \frac{\pi}{3} [\sigma_2^2 - (-1)^P \sigma_1^2] \left[\cos \frac{\pi}{3} I_1(\bar{x}_{02}) - \sin \omega_2 s_{02} I_0\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) \right].$$

In equations (5) and (6) we have adopted the convention that $(-1)^P$ is $+1$ if $P = \lambda$ and -1 if $P = \mu$. The quantities $I_j(\bar{x})$, ($j = 0, 1$), occurring in (5) and (6) are certain complicated integrals expressing the effect of the vibronic perturbation \mathcal{H}' (see Appendix I). The atomic overlap integrals s_{pq} and the geometrical factors $\cos \omega_j$ appear in equations (5) and (6) by virtue of our use of the SKLAR approximation to evaluate three-center integrals (see Appendix I).

Similarly the detailed evaluation of the integrals given in (2.3–11) yields, when substituted into equations (2.3–13, 14, 15 and 16), the results (see Appendices II and III).

$$\text{III} - E_u^0 \widetilde{\text{III}} = 6^{1/2} (a_{\text{III}} \mathcal{R}_{-2} + i b_{\text{III}} \mathcal{Y}_{-2}), \quad (2.4-7)$$

$$\text{III} - E_v^0 \widetilde{\text{III}} = 6^{1/2} (a_{\text{III}} \mathcal{R}_{-2} + i b_{\text{III}} \mathcal{Y}_{-2}), \quad (2.4-8)$$

where we have defined a_P and b_P , ($P = \text{III}, \text{III}$), as

$$a_P = \frac{1}{36} \left(k_{01} + 2 \sin \frac{\pi}{3} k_{02} - 8 k_{03} \right) - \frac{1}{6} [1 - (-1)^P] \left(k_{01} + 2 k_{02} \sin \frac{\pi}{3} + k_{03} \right)$$

$$- [\sigma_2^2 - (-1)^P \sigma_1^2] \left\{ 2 I_4(\bar{x}_{01}) + 4 \sin \frac{\pi}{3} I_4(\bar{x}_{02}) + 2 I_4(\bar{x}_{03}) - 2 \sin \frac{\pi}{3} I_5(\bar{x}_{02}) \right.$$

$$\left. - 2 \sin \frac{\pi}{3} I_3(\bar{x}_{02}) \left[I_6\left(\frac{1}{2} \bar{x}_{01}\right) + I_6\left(\frac{3}{2} \bar{x}_{01}\right) + 2 I_6\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) \right] \right.$$

$$\left. - I_2(\bar{x}_{02}) \left[I_4\left(\frac{3}{2} \bar{x}_{01}\right) - I_4\left(\frac{1}{2} \bar{x}_{01}\right) + 2 \cos \omega_1 I_4\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) \right] \right\}$$

$$- [\sigma_2^2 + (-1)^P \sigma_1^2] \left\{ 8 I_3(\bar{x}_{03}) I_6(\bar{x}_{01}) - 2 I_3(\bar{x}_{01}) \left[I_6\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) + I_6\left(\sqrt{\frac{13}{4}} \bar{x}_{01}\right) \right] - I_5(\bar{x}_{01}) + 2 I_5(\bar{x}_{03}) \right\}$$

$$\left\{ - 4 I_2(\bar{x}_{01}) \sin \frac{\pi}{3} \left[\sin \omega_1 I_4\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) + \cos \omega_4 I_4\left(\sqrt{\frac{13}{4}} \bar{x}_{01}\right) \right] \right\}$$

$$- \sigma_2^2 [\varepsilon_2^0 + 2 \gamma_{02}^0 + 3 \gamma_{12}^0 - \delta_{02}^0 + \delta_{-12}^0 - \delta_{12}^0 - w_{2p}^0 + (-1)^P (2 \eta^0 - \xi^0)] \left[2 I_3(\bar{x}_{03}) - 2 \sin \frac{\pi}{3} I_3(\bar{x}_{02}) - I_3(\bar{x}_{01}) \right]$$

$$+ (-1)^P \sigma_1^2 [\varepsilon_1^0 + 2 \gamma_{11}^0 + 2 \gamma_{01}^0 + \gamma_{12}^0 - \delta_{01}^0 - 2 \delta_{12}^0 - w_{2p}^0 + (-1)^P (\eta^0 - 2 \xi^0)]$$

$$\cdot \left[I_3(\bar{x}_{01}) - 2 \sin \frac{\pi}{3} I_3(\bar{x}_{02}) - 2 I_3(\bar{x}_{03}) \right] + \frac{1}{72} [1 - (-1)^P] \left(5 k_{01} + 10 k_{02} \sin \frac{\pi}{3} + 32 k_{03} \right), \quad (2.4-9)$$

$$\begin{aligned}
b_P = & -2 \sin \frac{\pi}{3} [\sigma_2^2 - (-1)^P \sigma_1^2] \left\{ I_3(\bar{x}_{02}) \left[I_6\left(\frac{1}{2} \bar{x}_{01}\right) + 2 I_6\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) + I_6\left(\frac{3}{2} \bar{x}_{01}\right) \right] + I_5(\bar{x}_{02}) \right. \\
& \left. + 2 \sin \frac{\pi}{3} I_2(\bar{x}_{02}) \left[I_4\left(\frac{1}{2} \bar{x}_{01}\right) - I_4\left(\frac{3}{2} \bar{x}_{01}\right) - 2 \cos \omega_1 I_4\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) \right] \right\} \\
& + 2 \sin \frac{\pi}{3} [\sigma_2^2 + (-1)^P \sigma_1^2] \left\{ 4 \sin \frac{\pi}{3} I_3(\bar{x}_{01}) \left[I_6\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) + I_6\left(\sqrt{\frac{13}{4}} \bar{x}_{01}\right) \right] + 2 \sin \frac{\pi}{3} I_5(\bar{x}_{01}) \right. \\
& \left. - 2 I_2(\bar{x}_{01}) \left[\sin \omega_1 I_4\left(\sqrt{\frac{7}{4}} \bar{x}_{01}\right) + \cos \omega_4 I_4\left(\sqrt{\frac{13}{4}} \bar{x}_{01}\right) \right] \right\} \\
& - 2 \sin \frac{\pi}{3} \sigma_2^2 [\varepsilon_2^0 + 2 \gamma_{02}^0 + 3 \gamma_{12}^0 - \delta_{02}^0 + \delta_{-12}^0 - \delta_{12}^0 - w_{2p}^0 + (-1)^P (2 \eta^0 - \xi^0)] [I_3(\bar{x}_{02}) - 2 \sin \frac{\pi}{3} I_3(\bar{x}_{01})] \\
& + 2 \sin \frac{\pi}{3} (-1)^P \sigma_1^2 [\varepsilon_1^0 + 2 \gamma_{11}^0 + 2 \gamma_{01}^0 + \gamma_{12}^0 - \delta_{01}^0 - 2 \delta_{12}^0 - w_{2p}^0 + (-1)^P (\eta^0 - 2 \xi^0)] \left[2 \sin \frac{\pi}{3} I_3(\bar{x}_{01}) + I_3(\bar{x}_{02}) \right] \\
& + 2 \sin \frac{\pi}{3} \left[\frac{1}{36} (2 \sin \frac{\pi}{3} k_{01} - k_{02}) + \frac{1}{72} [1 - (-1)^P] (10 \sin \frac{\pi}{3} k_{01} - 5 k_{02}) \right], \quad (2.4-10)
\end{aligned}$$

and where $(-1)^P$ is $+1$ if $P = \text{III}$ and -1 if $P = \text{III}$.

Now since the "mixing" coefficients C_{ST}' ($S, T = x, y, u, v$) are given as

$$C_{ST}' = - \frac{(S | \mathcal{H} - E_T^0 | T)'}{E_S^0 - E_T^0}, \quad (2.4-11)$$

it is convenient to define the quantities A and M such that

$$\begin{aligned}
(x | \mathcal{H} - E_u^0 | u)' &= \Re A = \Re (\lambda + \text{III} - E_u^0 \text{III}), \\
(x | \mathcal{H} - E_v^0 | v)' &= \Im M = \Im (\mu + \text{III} - E_v^0 \text{III}), \\
(y | \mathcal{H} - E_u^0 | u)' &= -\Im A = -\Im (\lambda + \text{III} - E_u^0 \text{III}), \\
(y | \mathcal{H} - E_v^0 | v)' &= \Re M = \Re (\mu + \text{III} - E_v^0 \text{III}).
\end{aligned} \quad (2.4-12)$$

In terms of the nuclear displacements R_r and Y_r these auxiliary functions A and M have the following values:

$$\begin{aligned}
A &= 6^{1/2} (A_A \mathcal{R}_{-2} + i B_A \mathcal{Y}_{-2}), \\
M &= 6^{1/2} (A_M \mathcal{R}_{-2} + i B_M \mathcal{Y}_{-2}),
\end{aligned} \quad (2.4-13)$$

where

$$\begin{aligned}
A_A &= a_\lambda + a_{\text{III}}, & B_A &= b_\lambda + b_{\text{III}}, \\
A_M &= a_\mu + a_{\text{III}}, & B_M &= b_\mu + b_{\text{III}}.
\end{aligned} \quad (2.4-14)$$

2.5 The Benzene Normal Co-ordinates of Species E_{2g}

Since, as we have seen in section 2.3, only the vibrations of symmetry species E_{2g} can "mix" the ${}^1E_{1u}$ with the (${}^1B_{1u}$, ${}^1B_{2u}$) benzene electronic states, we need compute only the normal co-ordinates of species E_{2g} . But because of insufficient experimental information relating to the ${}^1B_{1u}$ and ${}^1B_{2u}$ electronic states we shall use in our calculations the normal

co-ordinates of the ${}^1A_{1g}$ electronic configuration, i. e., of the electronic ground state. We shall, however, assign to these normal co-ordinates the frequencies observed in the ${}^1B_{2u}$ configuration (the normal frequencies of the ${}^1B_{1u}$ configuration have not as yet been determined). The effects of such approximations will be discussed at length in section 2.8.

In deriving the normal co-ordinates of species E_{2g} for the electronic ground state of benzene we have followed the well-known F , G , and L matrix technique of WILSON^{12, 20, 21}. As the F and G matrices for the E_{2g} vibrations of the benzene ${}^1A_{1g}$ electronic state have been computed by CRAWFORD and MILLER²², we needed only to compute the L matrix in order to relate the internal symmetry co-ordinates, $\mathcal{S}_{\xi t}$, ($t = a, b$), ($\xi = 6, 7, 8, 9$),

$$\begin{aligned}
\mathcal{S}_{6a} &= -2^{1/2} \Re \mathcal{A}_2 & \mathcal{S}_{6b} &= -2^{1/2} \Im \mathcal{A}_2 \\
\mathcal{S}_{7a} &= -2^{1/2} \Re \mathcal{P}_2 & \mathcal{S}_{7b} &= -2^{1/2} \Im \mathcal{P}_2 \\
\mathcal{S}_{8a} &= -2^{1/2} \Re (\omega \mathcal{N}_2) & \mathcal{S}_{8b} &= -2^{1/2} \Im (\omega \mathcal{N}_2) \\
\mathcal{S}_{9a} &= 2^{1/2} \Im \mathcal{B}_{-2} & \mathcal{S}_{9b} &= 2^{1/2} \Re \mathcal{B}_{-2}
\end{aligned} \quad (2.5-1)$$

where ($\omega = \exp[2\pi i/6]$)

$$\mathcal{A}_2 = x^0 6^{-1/2} \sum_{r=0}^5 (\omega^2)^r \alpha_r,$$

α_r = change in angle between C—C bonds r and $r+1$; x^0 being the equilibrium C—C bond length;

$$\mathcal{B}_{-2} = y^0 6^{-1/2} \sum_{r=0}^5 (\omega^{-2})^r \beta_r,$$

²⁰ E. B. WILSON, JR., J. Chem. Phys. **7**, 1047 [1939].

²¹ E. B. WILSON, JR., J. Chem. Phys. **9**, 76 [1941].

²² B. L. CRAWFORD and F. A. MILLER, J. Chem. Phys. **17**, 249 [1949].

β_r = change in the angle of the C-H bond with the exterior bisector of the C-C-C angle at the r^{th} C atom; y^0 being the equilibrium C-H bond length;

$$\mathcal{P}_2 = 6^{-1/2} \sum_{r=0}^5 (\omega^2)^r \varrho_r,$$

ϱ_r = change in the r^{th} C-H bond length;

$$\mathcal{N}_2 = 6^{-1/2} \sum_{r=0}^5 (\omega^2)^r \eta_r,$$

η_r = change in the r^{th} C-C bond length;

(2.5-2)

to the normal co-ordinates Q_{kt} , ($t=a, b$), ($k=6, 7, 8, 9$). The results of this calculation are:

$$(L) = \begin{pmatrix} 0.47912 & 0.24373 & 0.51619 & 0.26282 \\ -0.010185 & 1.03550 & -0.051420 & -0.017635 \\ 0.097510 & -0.062282 & -0.43033 & -0.097908 \\ -0.19289 & -0.065658 & -0.62798 & +0.83858 \end{pmatrix} \begin{matrix} 6 \\ 7 \\ 8 \\ 9 \end{matrix} \quad (2.5-3)$$

The substitution of (3) into the formula

$$\mathcal{S}_{\xi t} = \sum_{k=6}^9 L_{\xi k} Q_{kt} \quad (t=a, b), \quad (2.5-4)$$

then yields the desired relation between the internal symmetry co-ordinates $\mathcal{S}_{\xi t}$ and the normal co-ordinates Q_{kt} . In equation (4), (Q_{ka} , Q_{kb}) are the doubly degenerate pair of normal co-ordinates of symmetry E_{2g} which are associated with the normal frequency ν_k .

2.6 Matrix Elements Expressed in Terms of Normal Co-ordinates

According to (1.3-7 and 8) and (1.4-8 and 9), it is the matrix elements $(\Theta_l | \mathcal{H} - E_K^0 | \Theta_k)'$ which determine the extent of interaction of the benzene states (${}^1B_{1u}$, ${}^1B_{2u}$, and ${}^1E_{1u}$) and the intensity of the spectral transitions ${}^1A_{1g} \rightarrow ({}^1B_{1u}, {}^1B_{2u})$. Hence we desire to know the quantities,

$$\begin{aligned} A &= 6^{1/2} (A_A \mathcal{R}_{-2} + i B_A \mathcal{Y}_{-2}) = \lambda + \text{III} - E_u^0 \tilde{\text{III}}, \\ M &= 6^{1/2} (A_M \mathcal{R}_{-2} + i B_M \mathcal{Y}_{-2}) = \mu + \text{III} - E_v^0 \tilde{\text{III}}, \end{aligned} \quad (2.6-1)$$

rather than the values of (λ, μ) and $(\text{III}, \tilde{\text{III}}, \text{III}, \tilde{\text{III}})$ separately. In equation (1) we have designated the energy of the benzene states ${}^1B_{1u}$, and ${}^1B_{2u}$ by E_u^0

and E_v^0 , respectively (we shall later designate the energy of the ${}^1E_{1u}$ states as E_r^0); and have defined A_P and B_P ($P=A, M$) as

$$\begin{aligned} A_A &= a_\lambda + a_{\text{III}}, & B_A &= b_\lambda + b_{\text{III}}, \\ A_M &= a_\mu + a_{\text{III}}, & B_M &= b_\mu + b_{\text{III}}. \end{aligned} \quad (2.6-2)$$

It is now our task to express \mathcal{R}_{-2} and \mathcal{Y}_{-2} , and hence A and M , as functions of the normal co-ordinates (Q_k). We shall proceed to solve this problem by obtaining a relation between the $\mathcal{S}_{\xi a, b}$ of section 2.5 and $(\mathcal{R}_{-2}, \mathcal{Y}_{-2})$. A simple substitution into (2.5-4) then yields the desired result.

The relation we seek between $(\mathcal{R}_{-2}, \mathcal{Y}_{-2})$ and is most simply obtained by vectorial addition of their displacement diagrams. This procedure yields²³

$$\begin{aligned} \Re \mathcal{R}_{-2} &= (2/3)^{1/2} (3 \mathcal{S}_{6a} + 3^{1/2} \mathcal{S}_{8a}), \\ \Im \mathcal{R}_{-2} &= -(2/3)^{1/2} (3 \mathcal{S}_{6b} + 3^{1/2} \mathcal{S}_{8b}), \\ \Re \mathcal{Y}_{-2} &= (2/3)^{1/2} (\mathcal{S}_{6b} + 3^{1/2} \mathcal{S}_{8b}), \\ \Im \mathcal{Y}_{-2} &= (2/3)^{1/2} (\mathcal{S}_{6a} + 3^{1/2} \mathcal{S}_{8a}). \end{aligned} \quad (2.6-3)$$

The substitution of (2.5-4) into (3) then gives the sought result

$$\begin{aligned} \Re \mathcal{R}_{-2} &= (2/3)^{1/2} \sum_{k=6}^9 (3 L_{6k} + 3^{1/2} L_{8k}) Q_{ka}, \\ \Im \mathcal{R}_{-2} &= -(2/3)^{1/2} \sum_{k=6}^9 (3 L_{6k} + 3^{1/2} L_{8k}) Q_{kb}, \\ \Re \mathcal{Y}_{-2} &= (2/3)^{1/2} \sum_{k=6}^9 (L_{6k} + 3^{1/2} L_{8k}) Q_{kb}, \\ \Im \mathcal{Y}_{-2} &= (2/3)^{1/2} \sum_{k=6}^9 (L_{6k} + 3^{1/2} L_{8k}) Q_{ka}. \end{aligned} \quad (2.6-4)$$

The quantities A and M are now obtained by placing the results of equation (4) into equation (1): ($P=A, M$)

$$\begin{aligned} P &= 2 \sum_{k=6}^9 [(3 A_P - B_P) L_{6k} + 3^{1/2} (\bar{A}_P - \bar{B}_P) L_{8k}] Q_{ka} \\ &\quad - 2i \sum_{k=6}^9 [(3 A_P - B_P) L_{6k} + 3^{1/2} (\bar{A}_P - \bar{B}_P) L_{8k}] Q_{kb}. \end{aligned} \quad (2.6-5)$$

If we define for ($P=A, M$) and ($k=6, 7, 8, 9$) the quantity

$$D_{Pk} = 2(3 \bar{A}_P - \bar{B}_P) L_{6k} + 2(3)^{1/2} (\bar{A}_P - \bar{B}_P) L_{8k}, \quad (2.6-6)$$

²³ A. D. LIEHR, The Interaction of Vibrational and Electronic Motions in Some Conjugated Hydrocarbons, Thesis, Harvard University 1955. This thesis contains an intensity calculation based on eqn. (1.3-11), and a preliminary ac-

count of the theory of vibronic interactions in degenerate electronic states. Copies of this thesis are available from the author upon request.

we may write (5) in the more succinct form

$$P = \sum_{k=6}^9 D_{Pk} (Q_{ka} - i Q_{kb}), \quad (P = A, M). \quad (2.6-7)$$

2.7 Calculation of the Oscillator Strength of the Benzene ${}^1B_{1u}$ and ${}^1B_{2u}$ Ultra-Violet Band Systems

We first note that the spectral transitions ${}^1A_{1g} \rightarrow ({}^1B_{1u}, {}^1B_{2u})$ are electronically "forbidden" (recall section 1.4) since, on symmetry grounds,

$$\int \Theta_N^{0*} \mathfrak{M}_e \Theta_L^0 d\tau_{el} = 0 \quad (L = u, v). \quad (2.7-1)$$

Equation (1) follows by noting that since Θ_N^0 is of symmetry species A_{1g} , Θ_T^0 ($T = u, v$) of symmetry species (B_{1u}, B_{2u}) , and \mathfrak{M}_e (the electronic dipole moment) is of symmetry species E_{1u} , the integrand of (1) is not an invariant and so on integration must vanish identically. Hence equation (1.4-8) becomes for $(L = u, v)$:

$$\mathfrak{M}_{N0, L} = \int \Theta_N^{0*} \mathfrak{M}_e \Theta_X^0 d\tau_{el} \cdot \int N_0^{N*} C'_{XL} N_l^L d\tau_n + \int \Theta_N^{0*} \mathfrak{M}_e \Theta_y^0 d\tau_{el} \cdot \int N_0^{N*} C'_{yL} N_l^L d\tau_n. \quad (2.7-2)$$

Equation (2) gives the transition moment $\mathfrak{M}_{Kk, Ll}$ for the spectral transition from the vibrationally unexcited electronic state Θ_N (${}^1A_{1g}$) to the electronic state Θ_u (${}^1B_{1u}$) or Θ_v (${}^1B_{2u}$) with an arbitrary degree of vibrational excitation l . The remaining terms of equation (1.4-8) were dropped in (2) because $(L = u, v)$ implies

$$\int \Theta_I^{0*} \mathfrak{M}_e \Theta_L^0 d\tau_{el} = 0, \quad (I = N, x, y) \quad (2.7-3)$$

on grounds of symmetry alone; and because, for benzene, integrals of the form

$$\int \Theta_{N,T}^{0*} \mathfrak{M}_e \Theta_{T,N}^0 d\tau_{el} \cdot N_0^{N*} N_l^T d\tau_n$$

are very small (see section 2.8).

The choice of a "cold" electronic transition ${}^1A_{1g} \rightarrow {}^1B_{1u}, {}^1B_{2u}$ (that is, an electronic transition in which the initial state, here ${}^1A_{1g}$, is vibrationally unexcited) was made in order to obtain a temperature independent result. Since the relative population of the various vibrational levels in the initial electronic state ${}^1A_{1g}$ occur linearly in the intensity formulae^{12, 13}, one must multiply each vibrational transition by its BOLTZMAN factor. The BOLTZMAN factors are small (order of 0.06 at room temperature) for the excited vibrational states in the ${}^1A_{1g}$ electronic configuration; thus one may, to a good approximation, consider only the "cold" electronic transitions as was done in equation (2).

Now from (1.3-7 and 8) and (2.4-12) combined with (2.6-6 and 7) we have the relations

$$\begin{aligned} C'_{xu} &= -\frac{\Re A}{E_x^0 - E_u^0} = -\sum_{k=6}^9 \frac{D_{Ak} Q_{ka}}{E_x^0 - E_u^0}, \\ C'_{yu} &= +\frac{\Im A}{E_y^0 - E_u^0} = -\sum_{k=6}^9 \frac{D_{Ak} Q_{kb}}{E_y^0 - E_u^0}, \\ C'_{xv} &= -\frac{\Im M}{E_x^0 - E_v^0} = +\sum_{k=6}^9 \frac{D_{Mk} Q_{kb}}{E_x^0 - E_v^0}, \\ C'_{yv} &= -\frac{\Re M}{E_y^0 - E_v^0} = -\sum_{k=6}^9 \frac{D_{Mk} Q_{ka}}{E_y^0 - E_v^0}. \end{aligned} \quad (2.7-4)$$

Hence, to the first-order in the nuclear displacements, the vibronic perturbation allows only vibrational transitions in which there is absorbed one quantum of vibrational energy corresponding to an oscillation of symmetry E_{2g} . Moreover, the approximation of a cold electronic transition has the immediate consequence that the transitions ${}^1A_{1g} \rightarrow {}^1B_{1u}, {}^1B_{2u}$ are only allowed if the upper state ${}^1B_{1u}$ or ${}^1B_{2u}$ has a *singly* excited normal mode of symmetry species E_{2g} . Thus in equation (2) we can set $l = 1(k)$ and by use of (4) derive the result

$$\begin{aligned} \mathfrak{M}_{N0, ul} &= \mathfrak{M}_{N0, u1(k)} = \int \Theta_N^{0*} \mathfrak{M}_e \Theta_x^0 d\tau_{el} \cdot \left\{ -\frac{\sum_{k=6}^9 D_{Ak}}{E_x^0 - E_u^0} \int N_0^{N*} (Q_{ka} + Q_{kb}) N_{1(k)}^u d\tau_n \right\}, \\ \mathfrak{M}_{N0, vl} &= \mathfrak{M}_{N0, v1(k)} = \int \Theta_N^{0*} \mathfrak{M}_e \Theta_x^0 d\tau_{el} \cdot \left\{ -\frac{\sum_{k=6}^9 D_{Mk}}{E_x^0 - E_v^0} \int N_0^{N*} (Q_{ka} + Q_{kb}) N_{1(k)}^v d\tau_n \right\}. \end{aligned} \quad (2.7-5)$$

We have here used the fact that the two components (Θ_x, Θ_y) of the ${}^1E_{1u}$ electronic state have equal transition moments. Since only one normal mode $Q_{ka, b}$ may be excited in the states ${}^1B_{1u}$ and ${}^1B_{2u}$, we have finally, upon integration over the entire band system (this eliminates all the vibrational integrals except that over $Q_{ka, b}$):

$$\begin{aligned}\mathfrak{M}_{N0,u1(kP)} &= -\frac{(0|Q_{kP}|1)D_{Ak}}{E_x^0 - E_u^0} \int \Theta_N^{0*} \mathfrak{M}_e \Theta_x^0 d\tau_{el}. \\ \mathfrak{M}_{N0,v1(kP)} &= (-1)^P \frac{(0|Q_{kP}|1)D_{Mk}}{E_x^0 - E_v^0} \int \Theta_N^{0*} \mathfrak{M}_e \Theta_x^0 d\tau_{el},\end{aligned}\quad (2.7-6)$$

where $(-1)^P$ is -1 if $P=a$ and $+1$ if $P=b$.

Let us, without loss of generality, take the energy of the ground electronic state ${}^1A_{1g}$ to be the zero of energy. Then substituting (6) into equation (1.4-9), making use of the relation¹⁶

$$f_{N \rightarrow x} = f_{N \rightarrow y} = 1.085 \cdot 10^{11} \cdot \frac{|\int \Theta_N^{0*} \mathfrak{M}_e \Theta_x^0 d\tau_{el}|^2}{e^2} E_x^0 \text{ (cm}^{-1}\text{)}, \quad (2.7-7)$$

we obtain ($P=a, b$; $k=6, 7, 8, 9$):

$$\begin{aligned}f_{N0 \rightarrow u1(kP)} &= \frac{(0|Q_{kP}|1)^2 D_{Ak}^2 E_u^0}{(E_x^0 - E_u^0)^2 E_x^0} f_{N \rightarrow x}, \\ f_{N0 \rightarrow v1(kP)} &= \frac{(0|Q_{kP}|1)^2 D_{Mk}^2 E_v^0}{(E_x^0 - E_v^0)^2 E_x^0} f_{N \rightarrow x}.\end{aligned}\quad (2.7-8)$$

Using the numerical values of the integrals $I_j(\bar{x})$ ($j=0, 1, 2, 3, 4, 5, 6$) tabulated in appendix IV, the integrals γ_{ij}^0 , δ_{ij}^0 and ε_j^0 tabulated by PARR, CRAIG and ROSS¹⁸, the constants k_{ij} , etc. tabulated in Appendix IV, we have obtained the numerical values for the D_{Pk} ($P=A, M$) given in Table 1 (the numbers in parenthesis give the defining equations for the quantity tabulated).

Further, if one neglects the change in equilibrium internuclear distances in the excited state we may write (see section 2.8 for a discussion of this approximation):

$$(0|Q_{kP}|1) = \left(\frac{h N_0}{8 \pi^2 c \nu_k}\right)^{1/2} = 4.10568 \cdot 10^{-8} \bar{\nu}_k^{-1/2}, \quad (P=a, b),$$

where h is PLANCK's constant, c is the velocity of light, ν_k is the frequency in cm^{-1} , and N_0 is AVAGADRO's number. Thus using both the theoretical and experimental values of $f_{N \rightarrow x}$ and E_T^0 ($T=x, y, u, v$), and the experimental values of $\bar{\nu}_k$ for the ${}^1B_{2u}$ state

(see Table 2), we have the final theoretical results for the intensities of the ${}^1A_{1g} \rightarrow ({}^1B_{1u}, {}^1B_{2u})$ transitions of benzene as given in Table 3.

2.8 Discussion of Results

We see from Table 3 that although the absolute intensity of the transitions ${}^1A_{1g} \rightarrow ({}^1B_{1u}, {}^1B_{2u})$ agrees well with experiment, the distribution of intensity between the normal modes Q_{6t} and Q_{8t} ($t=a, b$), for the ${}^1B_{2u}$ state differs from the experimental value by a factor of three hundred. This discrepancy is not too surprising when one considers that this distribution depends rather critically on both the normal co-ordinates $Q_{k(a,b)}$, as described by the (L)

| | | | |
|--------------------------------|---------------------------------|--------------------------------|--------------------------------|
| $a_\lambda(2.4-5)$ -2.1303 | $b_\lambda(2.4-6)$ -7.0383 | $a_\mu(2.4-5)$ -2.2679 | $b_\mu(2.4-6)$ +5.0699 |
| $a_{III}(2.4-9)$ -2.1781 | $b_{III}(2.4-10)$ -6.6580 | $a_{III}(2.4-9)$ +1.3758 | $b_{III}(2.4-10)$ -6.7082 |
| $\bar{A}_A(2.4-14)$ -4.3084 | $\bar{B}_A(2.4-14)$ -13.6963 | $\bar{A}_M(2.4-14)$ -0.8921 | $\bar{B}_M(2.4-14)$ -1.6383 |
| $D_{A6}(2.6-6)$ +3.9100 | $D_{A7}(2.6-6)$ -1.6496 | $D_{A8}(2.6-6)$ -13.1986 | $D_{A9}(2.6-6)$ -2.7787 |
| $D_{M6}(2.6-6)$ -0.7427 | $D_{M7}(2.6-6)$ -0.6670 | $D_{M8}(2.6-6)$ -2.1840 | $D_{M9}(2.6-6)$ -0.7987 |

Tab. 1. Numerical Values of the Vibronic Constants in Units of $Z^2 e^2/a_0^2 \cdot 10^{-3}$.

| | | | |
|---|--|--|--|
| $\bar{\nu}_6(\text{expt'l})^{24}$ 521 cm^{-1} | $\bar{\nu}_7(\text{expt'l})^{24}$ 3080 cm^{-1} | $\bar{\nu}_8(\text{expt'l})^{24}$ 1470 cm^{-1} | $\bar{\nu}_9(\text{expt'l})^{24}$ 1130 cm^{-1} |
| $f_{N \rightarrow x} + f_{N \rightarrow y}(\text{expt'l})^{25}$ 0.88 | $f_{N \rightarrow x} + f_{N \rightarrow y}(\text{calc'd})^{26}$ 2.566 | $E_x^0 = E_y^0(\text{expt'l})^{18}$ 7.0 e.v. | $E_x^0 = E_y^0(\text{calc'd})^{18}$ 9.8 e.v. |
| $E_u^0(\text{expt'l})^{18}$ 6.2 e.v. | $E_u^0(\text{calc'd})^{18}$ 7.3 e.v. | $E_v^0(\text{expt'l})^{18}$ 4.9 e.v. | $E_v^0(\text{calc'd})^{18}$ 5.9 e.v. |

Tab. 2. Theoretical and Experimental Values of $\bar{\nu}_k$ ($k=6, 7, 8, 9$), $f_{N \rightarrow x}$, and E_T^0 ($T=x, y, u, v$).

| Calculated Using expt'l E_T^0 and $f_{N \rightarrow x}$ | | Calculated Using Theoretical E_T^0 and $f_{N \rightarrow x}$ | |
|---|---|---|---|
| $f_{N0 \rightarrow u1} = \sum_{k=6}^9 \frac{(2.7-8)}{f_{N0 \rightarrow u1}(k_{a,b})}$ | $f_{N0 \rightarrow v1} = \sum_{k=6}^9 \frac{(2.7-8)}{f_{N0 \rightarrow v1}(k_{a,b})}$ | $f_{N0 \rightarrow u1}$ | $f_{N0 \rightarrow v1}$ |
| 0.454 | 0.00318 | 0.257 | 0.00269 |
| $f_{N0 \rightarrow u1}(6)/f_{N0 \rightarrow u1}(8)$ | $f_{N0 \rightarrow v1}(6)/f_{N0 \rightarrow v1}(8)$ | $f_{N0 \rightarrow u1}(6)/f_{N0 \rightarrow u1}(8)$ | $f_{N0 \rightarrow v1}(6)/f_{N0 \rightarrow v1}(8)$ |
| 0.427 | 0.326 | 0.248 | 0.326 |
| $f_{N0 \rightarrow u1} \text{ (expt'l)}^{25}$ | $f_{N0 \rightarrow v1} \text{ (expt'l)}^{27}$ | $f_{N \rightarrow x} + f_{N \rightarrow y} \text{ (expt'l)}^{25}$ | $\frac{f_{N0 \rightarrow v1}(6)}{f_{N0 \rightarrow v1}(8)} \text{ (expt'l)}^{24}$ |
| 0.094 | 0.0014 | 0.88 | ~ 100 |

Tab. 3. Theoretical Results for the Intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$, ${}^1B_{2u}$ Spectral Transitions.

matrix, and on differences of the vibronic interaction constants \bar{A}_P and \bar{B}_P ($P=A, M$) (see equations 2.6–6 and 2.7–8). As we have not used the correct normal co-ordinates for the excited states ${}^1B_{1u}$ and ${}^1B_{2u}$, but have approximated them by those calculated for the ground state ${}^1A_{1g}$, we cannot expect that the relative magnitudes of the matrix elements L_{jk} , ($j, k=6, 8$), of the ${}^1B_{1u}$ and ${}^1B_{2u}$ electronic states have been properly assessed. Also, since the vibronic interactions \bar{A}_P and \bar{B}_P ($P=A, M$) have been computed by use of the SKLAR²⁸ approximation for three and four center integrals and the PARR²⁹ approximation for electron correlation integrals, these quantities are only correct as to order of magnitude. Hence, quantities, such as the vibrational-intensity distribution, which depend on weight-

ed differences of \bar{A}_P and \bar{B}_P ($P=A, M$) can be expected to be in error by a non-trivial amount.

We also see from Table 3 that the intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition is too large by a factor of two and a half. This discrepancy is undoubtedly due to the neglect of terms of second-order in the nuclear displacements, as these terms are not negligible when the corresponding first-order terms are as large as those of the ${}^1B_{1u}$ electronic state (see Table 1). Since the labor required to include the second-order terms is prohibitively large, we have not attempted to refine the first-order result given in Table 3.

In section 2.7 we neglected terms of the type ($L=u, v$)

$$\begin{aligned} \int N_0^{N*} \int \Theta_N' \mathfrak{M}_e \Theta_L^0 d\tau_{el} N_l^L d\tau_n &= \sum_a \int \Theta_L^0 \mathfrak{M}_e (\nabla_{\mathbf{s}_a=0}^{\rightarrow} \Theta_N \cdot \int N_0^{N*} \hat{s}_a N_l^L d\tau_n) d\tau_{el}, \\ \int N_0^{N*} \int \Theta_N^{0*} \mathfrak{M}_e \Theta_L' d\tau_{el} N_l^L d\tau_n &= \sum_a \int \Theta_N^{0*} \mathfrak{M}_e (\nabla_{\mathbf{s}_a=0}^{\rightarrow} \Theta_L \cdot \int N_0^{N*} \hat{s}_a N_l^L d\tau_n) d\tau_{el}. \end{aligned} \quad (2.8-1)$$

on the grounds that they are very small. The contributions of the integrals given by equation (4) to the intensity, had they been included in (2.7–2), is of the order of 10^{-2} to 10^{-3} times the experimental values for the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition, as was first shown by SPONER and HERZFELD³⁰. This was to be expected since such terms represent only the change in magnitude of the elementary dipole mo-

ment integral

$$\int \Theta_N^* N_0^{N*} \mathfrak{M}_e \Theta_L N_l^L d\tau_n d\tau_{el}, \quad (L=u, v), \quad (2.8-2)$$

from the zero value attained at the equilibrium nuclear configuration.

Also, in equation (2.7–9), we have neglected to include the vibrational overlap integral which arises

²⁴ F. M. GARFORTH, C. K. INGOLD and H. G. POOLE, J. Chem. Soc. **1**, 505 [1948].

²⁵ V. J. HAMMOND and W. C. PRICE, Trans. Faraday Soc. **51**, 605 [1955].

²⁶ C. W. L. BEVAN and D. P. CRAIG, Trans. Faraday Soc. **47**, 564 [1951].

²⁷ H. B. KLEVEN and J. R. PLATT, Technical Report of the Laboratory of Molecular Structure and Spectra, University of Chicago 1953/54.

²⁸ A. L. SKLAR, J. Chem. Phys. **7**, 984 [1939].

²⁹ R. G. PARR, J. Chem. Phys. **20**, 1499 [1952].

³⁰ H. SPONER and K. F. HERZFELD, Z. Phys. **133**, 41 [1952].

Using (7) in (6) yields $\left(\text{since } d\tau_{e1} = d\tau \left(\frac{a_0}{Z} \frac{\vec{r}}{\varrho} \right) = \left(\frac{a_0}{Z} \right)^3 d\sigma d\beta \right)$

$$(0|1|0) = \frac{Z^2 e^2}{a_0^2} N^2 \int d\beta d\sigma_{01} e^{-\varrho_0} \sin^2 \alpha_1 \cos^2 \beta \varrho_1^2 g_1(\varrho_1, \alpha_1, \beta) \cos \alpha_1 [R_1 \cos \pi/3 + Y_1 \sin \pi/3], \quad (\text{A1-8})$$

where N^2 is $(a_0/Z)^3 N_0^2$ (that is, N^2 equals $1/32\pi$). The terms containing $\sin \beta$ have been dropped in (8) since the integrand for these terms is of the form

$$\int_0^{2\pi} \cos^{2l} \beta \sin \beta d\beta = 0. \quad (\text{A1-9})$$

Defining $I_0(\bar{x}_{rt})$ as

$$I_0(\bar{x}_{rt}) = \frac{Z^2 e^2}{a_0^2} N_0^2 \int d\beta d\sigma_{rt} e^{-\varrho_t} \sin^2 \alpha_r \cos \alpha_r \cos^2 \beta \varrho_r^2 g_r(\varrho_r, \alpha_r, \beta), \quad (\text{A1-10})$$

we have finally

$$(0|1|0) = (R_1 \cos \pi/3 + Y_1 \sin \pi/3) I_0(\bar{x}_{01}). \quad (\text{A1-11})$$

Proceeding analogously for the other integrals, we obtain the results given in reference²³. The summation of integrals such as those of equation (11) then yields the diagonal terms of equation (2.3-10) as

$$\sum_{r=0}^5 (\omega^{-2})^r h'_{rr} = 6^{1/2} \mathcal{R}_{-2} [I_0(\bar{x}_{03}) - \cos \pi/3 I_0(\bar{x}_{01}) - \sin \pi/3 I_0(\bar{x}_{02})] + 2i 6^{1/2} \sin \pi/3 \mathcal{Y}_{-2} [\sin \pi/3 I_0(\bar{x}_{01}) - \cos \pi/3 I_0(\bar{x}_{02})], \quad (\text{A1-12})$$

the quantities \mathcal{R}_{-2} and \mathcal{Y}_{-2} being defined as in equations (2.4-3 and 4).

h'_{rt} Integrals with r+t odd:

The first integral of this type is

$$(0|0|1) = \frac{Z^2 e^2}{a_0^2} N_0^2 \int \varrho_0 \varrho_1 e^{-(\varrho_0 + \varrho_1)/2} \cos \vartheta_0 \cos \vartheta_1 \sin \vartheta_0 g_0(\varrho_0, \vartheta_0) [R_0 \sin \varphi_0 + Y_0 \cos \varphi_0] d\tau_{e1}, \quad (\text{A1-13})$$

which when transformed as in (7) and (8) becomes

$$(0|0|1) = \frac{Z^2 e^2}{a_0^2} N^2 \int d\sigma_{01} d\beta \sin^2 \alpha_0 \varrho_0^2 e^{-1/2(\varrho_0 + \varrho_1)} \cos \alpha_0 \cos^2 \beta g_0(\varrho_0, \alpha_0, \beta) [R_0 \cos \pi/3 - Y_0 \sin \pi/3]. \quad (\text{A1-14})$$

Defining $I_1(\bar{x}_{rt})$ as

$$I_1(\bar{x}_{rt}) = \frac{Z^2 e^2}{a_0^2} N^2 \int d\sigma_{rt} d\beta \sin^2 \alpha_r \cos \alpha_r \varrho_r^2 e^{-1/2(\varrho_r + \varrho_t)} g_r(\varrho_r, \alpha_r, \beta) \cos^2 \beta, \quad (\text{A1-15})$$

we have the desired result

$$(0|0|1) = (\cos \pi/3 R_0 - \sin \pi/3 Y_0) I_1(\bar{x}_{01}). \quad (\text{A1-16})$$

The case of $(0|2|1)$ is slightly different since it is a three center integral. We shall use the SKLAR approximation²⁸ in integrating it. To a fair approximation

$$(p|r|q) \approx s_{pq} (p'|r|p'), \quad (\text{A1-17})$$

where $\Phi_{p'}$ is a $2p_z$ carbon atomic orbital centered at a position midway between p and q , and s_{pq} in the overlap integral between the original orbitals Φ_p and Φ_q . For example, we have for $(0|2|1)$,

$$(0|2|1) \approx s_{01} (0'|2|0'). \quad (\text{A1-18})$$

In (18) the bipolar co-ordinate diagram appears as shown in Fig. 3.

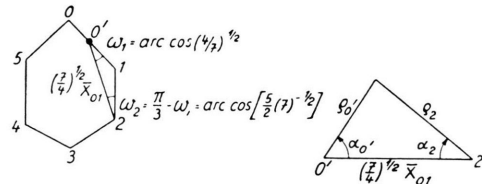


Fig. 3. Coordinate System for the Evaluation of the Matrix Element $(0'|2|0')$.

Thus (18) may be written in the form

$$(0|2|1) \approx s_{01} (0'|2|0') = (R_2 \cos \omega_1 + Y_2 \sin \omega_1) s_{01} I_0[(7/4)^{1/2} \bar{x}_{01}]. \quad (\text{A1-19})$$

By analogous means we may find the remaining integrals $(r|a|t)$, $r+t$ odd. These integrals when substituted into the corresponding terms of equations (2.3-10) yield²³

$$\sum_{\substack{r,t \\ r+t \text{ odd}}} (\omega^2)^{r+t} h'_{rt} = 2(6)^{1/2} \mathcal{R}_{-2} \{ I_1(\bar{x}_{03}) - \cos \pi/3 I_1(\bar{x}_{01}) - \cos \omega_3 s_{01} I_0[(\frac{1}{4})^{1/2} \bar{x}_{01}] + 2 \cos \omega_1 s_{01} I_0[(\frac{1}{4})^{1/2} \bar{x}_{01}] - s_{03} I_0(\bar{x}_{01}) \} \\ + 4i 6^{1/2} \sin \pi/3 \mathcal{Y}_{-2} \{ \sin \omega_3 s_{01} I_0[(\frac{1}{4})^{1/2} \bar{x}_{01}] - \sin \pi/3 I_1(\bar{x}_{01}) \}, \quad (\text{A1-20})$$

where $\omega_3 = \arccos[7(13)^{1/2}/26]$.

h'_{rt} Integrals with $r+t$ even:

The methods used to evaluate these integrals are the same as those used for h'_{rr} and for h'_{rt} with $r+t$ odd. Hence we may write²³

$$\sum_{\substack{r,t \\ r+t \text{ even}}} (\omega^2)^{r+t} h'_{rt} = 2(6)^{1/2} \mathcal{R}_{-2} \{ s_{02} I_0(\frac{1}{2} \bar{x}_{01}) + s_{02} I_0(\frac{3}{2} \bar{x}_{01}) - \cos \omega_2 s_{02} I_0[(\frac{1}{4})^{1/2} \bar{x}_{01}] - \sin \pi/3 I_1(\bar{x}_{02}) \} \\ + 4i \sin \pi/3 6^{1/2} \mathcal{Y}_{-2} \{ \cos \pi/3 I_1(\frac{3}{2} \bar{x}_{01}) - \sin \omega_2 s_{02} I_0[(\frac{1}{4})^{1/2} \bar{x}_{01}] \}. \quad (\text{A1-21})$$

APPENDIX II

Calculation of the Matrix Elements $S'_{-2,2}$ and $S'_{1,-1}$

$$\text{Since by definition } S'_{ij} \text{ is given by } S'_{ij} = \sum_a \mathbf{s}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} \left\{ \int \psi_i^* \psi_j d\tau_{\text{el}} \right\}, \quad (\text{A2-1})$$

$$\text{direct integration yields } S'_{-2,2} = \sigma_2^2 \sum_{r,t} (\omega^2)^{r+t} (r|t)', \quad (\text{A2-2})$$

$$S'_{1,-1} = \sigma_1^2 \sum_{r,t} (-1)^{r+t} (\omega^2)^{r+t} (r|t)', \quad (\text{A2-3})$$

$$\text{where } (r|t)' = (r'|t) + (r|t') = \left\{ \int \Phi_r \Phi_t d\tau_{\text{el}} \right\}'. \quad (\text{A2-4})$$

It is convenient for later work to define the corresponding unprimed equation (4) in terms of the integral $I_2(\bar{x}_{rt})$,

$$I_2(\bar{x}_{rt}) = N^2 \int q_r q_t e^{-\frac{1}{2}(q_r + q_t)} \sin \alpha_r \sin \alpha_t \cos^2 \beta d\sigma_{rt} d\beta. \quad (\text{A2-5})$$

$$\text{Thus we have for this case } s_{rt} = (r|t) = I_2(\bar{x}_{rt}). \quad (\text{A2-6})$$

Now by use of equation (1.2-5) we may derive

$$\Phi_r'(\vec{q}_r, \mathbf{s}_r) = \sum_a \mathbf{s}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} \Phi_r(\vec{q}_r, \mathbf{s}_r) = -N_0 (\mathbf{s}_r \cdot \mathbf{f}) e^{-\frac{1}{2} q_r} + \frac{\vec{q}_r \cdot \mathbf{s}_r}{2 q_r} \Phi_r(\vec{q}_r). \quad (\text{A2-7})$$

The substitution of (7) into a portion of equation (4) then yields

$$(r|t') = \int \Phi_r^0 \Phi_t' d\tau_{\text{el}} = \frac{Z N_0^2}{2 a_0} \int d\tau_{\text{el}} q_r \cos \vartheta_r q_t \cos \vartheta_t e^{-\frac{1}{2}(q_r + q_t)} [R_t \sin \varphi_t + Y_t \cos \varphi_t] \sin \vartheta_t. \quad (\text{A2-8})$$

Letting $I_3(\bar{x}_{rt})$ be given by

$$I_3(\bar{x}_{rt}) = -\frac{Z N_0^2}{2 a_0} \int d\tau_{\text{el}} d\beta q_t^2 \sin^2 \alpha_t \cos \alpha_t \cos^2 \beta e^{-\frac{1}{2}(q_r + q_t)}, \quad (\text{A2-9})$$

we then have, for example,

$$(0|1)' = [(R_0 + R_1) \cos \pi/3 + (Y_1 - Y_0) \sin \pi/3] I_3(\bar{x}_{01}). \quad (\text{A2-10})$$

The remaining integrals $(r|t)'$ are obtained analogously²³, if one remembers that terms containing $\mathbf{s}_r \cdot \mathbf{f}$ vanish identically on integration, and that integrals of the form $(r|r)'$ vanish upon integration over the azimuthal angle. Then the substitution of the integrals $(r|t)'$ thus obtained yields the desired results

$$S'_{-2,2} = 6^{1/2} \sigma_2^2 \mathcal{R}_{-2} [2 I_3(\bar{x}_{03}) - 2 \sin \pi/3 I_3(\bar{x}_{02}) - I_3(\bar{x}_{01})] + 2i \sin \pi/3 (6)^{1/2} \sigma_2^2 \mathcal{Y}_{-2} [I_3(\bar{x}_{02}) - 2 \sin \pi/3 I_3(\bar{x}_{01})], \quad (\text{A2-11})$$

$$S'_{1,-1} = 6^{1/2} \sigma_1^2 \mathcal{R}_{-2} [I_3(\bar{x}_{01}) - 2 \sin \pi/3 I_3(\bar{x}_{02}) - 2 I_3(\bar{x}_{03})] + 2i \sin \pi/3 (6)^{1/2} \sigma_1^2 \mathcal{Y}_{-2} [2 \sin \pi/3 I_3(\bar{x}_{01}) + I_3(\bar{x}_{02})]. \quad (\text{A2-12})$$

The required vibronic interaction, induced by the terms $S'_{-2,2}$ and $S'_{1,-1}$, is readily computed by multiplying equations (11) and (12) by the GOEPPERT-MAYER and SKLAR formulae¹⁷ for E_u^0 and E_v^0 :

$$E_u^0 = 2\epsilon_0^0 + 3\epsilon_1^0 + \epsilon_2^0 + \gamma_{00}^0 + 6\gamma_{01}^0 + 2\gamma_{02}^0 + 3\gamma_{11}^0 + 3\gamma_{12}^0 - 3\delta_{01}^0 - \delta_{02}^0 - \delta_{1,-1}^0 + \delta_{-12}^0 - \delta_{12}^0 - \xi^0 + 2\eta^0, \quad (\text{A2-13})$$

$$E_v^0 = 2\epsilon_0^0 + 3\epsilon_1^0 + \epsilon_2^0 + \gamma_{00}^0 + 6\gamma_{01}^0 + 2\gamma_{02}^0 + 3\gamma_{11}^0 + 3\gamma_{12}^0 - 3\delta_{01}^0 - \delta_{02}^0 - \delta_{1,-1}^0 + \delta_{-12}^0 - \delta_{12}^0 + \xi^0 - 2\eta^0. \quad (\text{A2-14})$$

APPENDIX III

Calculation of the Matrix Elements $H_{ij}^{0'}$ ($i, j = \pm 1, \pm 2, \pm 3, \pm 4$)

We have seen in section 2.3 that the "overlap" matrix $(P|\mathcal{H}_0 - E_T^0|T)'$, ($P, T = u, v, x, y$) is determined by the integrals $H_{ij}^{0'}$ and S_{ij}' , where

$$H_{ij}^{0'} = \sum_a \mathbf{s}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} \left\{ \int \Theta_i^* \mathcal{H}_0 \Theta_j d\tau_{el} \right\}, \quad (\text{A3-1})$$

and where S_{ij}' is as given in Appendix II. Thus before we can compute the "overlap" matrix we must evaluate equation (1). This evaluation is best illustrated by considering a specific example, say $H_{31}^{0'}$,

$$H_{31}^{0'} = \left\{ \int \psi_0^*(1) \bar{\psi}_0^*(2) \psi_1^*(3) \psi_1^*(4) \psi_{-1}^*(5) \bar{\psi}_{-2}^*(6) \mathcal{H}_0 \sum_P (-1)^P \psi_0(1) \bar{\psi}_0(2) \psi_1(3) \bar{\psi}_1(4) \psi_{-1}(5) \bar{\psi}_2(6) d\tau_{el} \right\}'. \quad (\text{A3-2})$$

Using the spin and orbit orthogonality of the *equilibrium* molecular orbitals ψ_j^0 ($j=0, \pm 1, \pm 2$) we then have

$$H_{31}^{0'} = S_{-22}' (2\varepsilon_0^0 + 3\varepsilon_1^0 + \gamma_{00}^0 + 3\gamma_{11}^0 + 6\gamma_{01}^0 - 3\delta_{01}^0 - \delta_{1-1}^0) - S_{1-1}' \varepsilon_0^0 + \varepsilon_{-22}' + (2\xi_{22}^{00} - \xi_{02}^{02} + 3\xi_{22}^{1-1} - \xi_{12}^{-12})', \quad (\text{A3-3})$$

where ξ_{kl}^{ij} and ε_{ij} are as given in section 2.3. Similarly, as a further example, we have

$$H_{32}^{0'} = (\xi_{12}^{-12})' + S_{1-1}' \eta^0. \quad (\text{A3-4})$$

Evaluation of the Integrals $(\xi_{kl}^{ij})'$:

As an example of the evaluation of these integrals, we shall consider the special case of $(\xi_{22}^{00})'$,

$$(\xi_{22}^{00})' = \left\{ \iint \psi_0(1) \psi_0(1) \frac{e^2}{r_{12}} \psi_2(2) \psi_2(2) d\tau_1 d\tau_2 \right\}'. \quad (\text{A3-5})$$

Defining $(rs|pq)$ as

$$(rs|pq) = \int \Phi_r(1) \Phi_s(1) \frac{e^2}{r_{12}} \Phi_p(2) \Phi_q(2) d\tau_1 d\tau_2, \quad (\text{A3-6})$$

we may reduce (5) to

$$(\xi_{22}^{00})' = \sum_{r,s,p,q} \sigma_0^2 \sigma_2^2 (\omega^2)^{p+q} (rs|pq)'. \quad (\text{A3-7})$$

To proceed further we make use of the PARR approximation²⁹ for evaluating the integrals $(rs|pq)$. This approximation sets the functional product $\Phi_p \Phi_q$ equal to zero if $p \neq q$ (hence, the normalizing factor σ_ξ^2 becomes $1/6$, ($\xi=0, \pm 1, \pm 2, \pm 3$)) and thus concerns itself with only the evaluation of the COULOMB integrals $(pp|qq)$. These COULOMB integrals are then equated to the classical COULOMBIC interaction of two pairs of tangent, uniformly charged, non-conducting spheres of diameter R_p and charge $1/2 e$, at a distance r apart. Hence we may write²⁹

$$(\bar{R}_p = ZR_p/a_0, \bar{r} = Zr/a_0) : (pp|qq) = Ze^2/2\bar{r} [1 + \bar{R}_p^2/\bar{r}^2]^{-1/2}. \quad (\text{A3-8})$$

The undetermined diameter R_p is chosen as the equilibrium bond distance of the benzene ground electronic state²⁹. In terms of the notation of section 2.2 and Appendices I and II, the distance \bar{r} , which describes the separation of atoms p and q , is given by

$$\bar{r} = |\bar{x}_{pq} + \mathbf{s}_q - \mathbf{s}_p|. \quad (\text{A3-9})$$

Therefore, the integrals $(pp|qq)'$ are given by

$$(pp|qq)' = \sum_a \mathbf{s}_a \cdot \overrightarrow{\nabla_{\mathbf{s}_a=0}} (pp|qq) = k_{pq} (\mathbf{s}_q - \mathbf{s}_p) \cdot \frac{\bar{x}_{pq}}{|\bar{x}_{pq}|}, \quad (p \neq q), \quad (\text{A3-10})$$

where

$$k_{pq} = k(\bar{x}_{pq}) = -\frac{Z^2 e^2}{2 \bar{x}_{pq}^2 a_0^2} \left[1 + \left(1 + \bar{R}_p^2/\bar{x}_{pq}^2 \right)^{-1/2} - \bar{R}_p^2/\bar{x}_{pq}^2 \left(1 + \bar{R}_p^2/\bar{x}_{pq}^2 \right)^{-3/2} \right].$$

In equations (9) and (10), the unit vectors $\mathbf{r}_{pq}/|\mathbf{r}_{pq}|$ are directed from atom p to atom q . The integrals $(pp|pp)'$ vanish as the COULOMB integral $(pp|pp)$ is a constant independent of \mathfrak{s}_p .

Substituting (10) into (7) we then have the desired result

$$\begin{aligned} (\zeta_{22}^{00})' &= \frac{1}{36} \sum_{r,s,p,q} (\omega^2)^{p+q} (rr|pp)' \delta_{rs} \delta_{pq} = \frac{1}{36} \sum_{r,p} (\omega^2)^p (rr|pp)' \\ &= \frac{6^{1/2}}{36} \{ \mathcal{R}_{-2} [\cos \pi/3 k_{01} + \sin \pi/3 k_{02} + 2 k_{03}] + 2i \sin \pi/3 \mathcal{Y}_{-2} [k_{01} \sin \pi/3 - k_{02} \cos \pi/3] \}. \end{aligned} \quad (\text{A3-12})$$

In deriving (12) we have made use of unit vector identities such as

$$\mathfrak{x}_{r,r+1} = \Re_{r+1} \cos \pi/3 + \Im_{r+1} \sin \pi/3 = -\Re_r \cos \pi/3 + \Im_r \sin \pi/3, \quad (\text{A3-13})$$

where the German lettering indicates a unit vektor along the corresponding Roman letter co-ordinate. Similarly we may derive

$$\begin{aligned} (\zeta_{02}^{02})' &= \frac{6^{1/2}}{18} \{ \mathcal{R}_{-2} [k_{03} - k_{01} \cos \pi/3 - k_{02} \sin \pi/3] + 2i \sin \pi/3 \mathcal{Y}_{-2} [k_{02} \cos \pi/3 - k_{01} \sin \pi/3] \}, \\ (\zeta_{01}^{01})' &= \frac{6^{1/2}}{18} \{ \mathcal{R}_2 [k_{01} \cos \pi/3 - k_{02} \sin \pi/3 - k_{03}] - 2i \sin \pi/3 \mathcal{Y}_2 [k_{01} \sin \pi/3 + k_{02} \cos \pi/3] \}, \\ (\zeta_{12}^{-12})' &= \frac{6^{1/2}}{36} \{ \mathcal{R}_{-2} [k_{02} \sin \pi/3 - 2k_{03} - k_{01} \cos \pi/3] - 2i \sin \pi/3 \mathcal{Y}_{-2} [k_{01} \sin \pi/3 + k_{02} \cos \pi/3] \}, \\ (\zeta_{11}^{00})' &= (\zeta_{11}^{1-1})' = (\zeta_{2-2}^{11})' = (\zeta_{22}^{00})'^* = (\zeta_{22}^{00})'^*, \quad (\zeta_{12}^{1-2})' = (\zeta_{12}^{-12})'^*. \end{aligned} \quad (\text{A3-14})$$

Evaluation of the Integrals ε_{ij}' :

To illustrate the evaluation of these integrals we shall compute explicitly the term ε_{-22}' ,

$$\varepsilon_{-22}' = \left\{ \int \psi_{-2}^*(1) [\mathcal{T}_e(1) + \mathcal{V}_{e-n}^0(1)] \psi_2(1) d\tau_1 \right\}'. \quad (\text{A3-15})$$

Recalling the definition of $\mathcal{V}_{e-n}^0(1)$ — given in section 2.2, we may write

$$\mathcal{V}_{e-n}^0(1) = \sum_a \mathcal{V}_{e-n}^{(a)0}(1), \quad (\text{A3-16})$$

where $\mathcal{V}_{e-n}^{(a)0}(1)$ satisfies the relations¹⁷ (see section 2.2)

$$\mathcal{V}_{e-n}^{(a)0}(1) = \overline{\mathcal{V}}_{e-n}^{(a)0}(1) - e^2 \int \frac{[\Phi_a^0(2)]^2}{r_{12}} d\tau_2, \quad (\text{A3-17})$$

$$[\mathcal{T}_e(1) + \mathcal{V}_{e-n}^{(a)0}(1)] \Phi_a^0(1) = W_{2p}^0 \Phi_a^0(1), \quad (\text{A3-18})$$

w_{2p}^0 being the energy of the $2p_z$ electron of a carbon atom in its sp^3 valence state. Hence, ε_{-22}' may be expanded to read as follows:

$$\varepsilon_{-22}' = \sum_{r,t} (\omega^2)^{r+t} \int \left[\Phi_r' \left(\mathcal{T}_e + \sum_a \mathcal{V}_{e-n}^{(a)0} \right) \Phi_t^0 + \Phi_r^0 \left(\mathcal{T}_e + \sum_a \mathcal{V}_{e-n}^{(a)0} \right) \Phi_t' \right] d\tau_{el}, \quad (\text{A3-19})$$

$$\begin{aligned} \varepsilon_{-22}' &= \sum_{r,t} (\omega^2)^{r+t} \sigma_2^2 \left[w_{2p}^0(r'|t^0) - \sum_{p \neq t} (p^0:r't^0) + w_{2p}^0(r^0|t') - \sum_{p \neq r} (p^0:r^0t') \right. \\ &\quad \left. - \sum_{p \neq t} (p^0 p^0 | r't^0) - \sum_{p \neq r} (p^0 p^0 | r^0 t') \right], \end{aligned} \quad (\text{A3-20})$$

where

$$(p^0:r't^0) = - \int \Phi_r' \overline{\mathcal{V}}_{e-n}^{(p)0} \Phi_t^0 d\tau_{el}. \quad (\text{A3-21})$$

Collecting terms in (20), we have finally

$$\begin{aligned} \varepsilon_{-22}' &= w_{2p}^0 \mathcal{S}_{-22}' - \sigma_2^2 \left[\sum_r (\omega^2)^r \sum_{p \neq r} (p^0:rr)' + \sum_{r \neq t} (\omega^2)^{r+t} \sum_{p \neq r, p \neq t} (p^0:rt)' + 2 \sum_{r \neq t} (\omega^2)^{r+t} (r^0:r't^0) \right. \\ &\quad \left. + 2 \sum_{r \neq t} (\omega^2)^{r+t} (r^0 r^0 | r't^0) + \sum_{\substack{r,t,p \\ p \neq r, p \neq t}} (\omega^2)^{r+t} (p^0 p^0 | rt)' \right]. \end{aligned} \quad (\text{A3-22})$$

The PARR approximation²⁹ applied to the terms $(r^0 r^0 | r't^0)'$ and $(p^0 p^0 | rt)'$ of equation (22) yields (note that since atom p is here fixed, \mathfrak{s}_p must vanish):

$$\sigma_2^2 \sum_{\substack{r, t, p \\ p \neq t, p \neq r}} (\omega^2)^{r+t} (p^0 p^0 | rt)' = 6^{-1/2} \mathcal{R}_{-2} [2k_{01} \cos \pi/3 + 2k_{02} \sin \pi/3 + k_{03}], \quad (\text{A3-23})$$

$$\sigma_2^2 \sum_{r \neq t} (\omega^2)^{r+t} (r^0 r^0 | rt^0)' = 0 \text{ (since } \Phi_r \Phi_t = 0, r \neq t). \quad (\text{A3-24})$$

The evaluation of the remaining terms of (22) is more difficult. In the following paragraphs, we shall outline the procedure employed in their evaluation.

Now since $(p^0 : rr)'$ is equal to $2(p^0 : r'r^0)$, the first terms of (22) may be written as [using eq. (A2-7)]

$$(p^0 : r^0 r') = - \int \Phi_r^0 \bar{\Psi}_{e-n}^{(p)0} \Phi_r' d\tau_{el} = - \int d\tau_{el} \Phi_r^0 \left[\frac{1}{2} \bar{\Psi}_{e-n}^{(p)0} \right] \vec{Q}_r \cdot \mathbf{s}_r / Q_r \Phi_r^0. \quad (\text{A3-25})$$

Thus defining $I_4(\bar{x}_{rp})$ as

$$I_4(\bar{x}_{rp}) = \int \Phi_r^0 \left[Z/2 a_0 \bar{\Psi}_{e-n}^{(p)0} \right] \cos \alpha_r \Phi_r^0 d\tau_{el}, \quad (\text{A3-26})$$

we may re-write (25) to read

$$(p^0 : r^0 r') = - [R_r \cos(\xi_{rp}, \Re_r) + Y_r \cos(\xi_{rp}, \Im_r)] I_4(\bar{x}_{rp}). \quad (\text{A3-27})$$

Employing (27) in (22) we then have

$$\sum_r (\omega^2)^r \sum_{p \neq r} (p^0 : rr)' = 2(6)^{1/2} \mathcal{R}_{-2} [2I_4(x_{01}) \cos \pi/3 + 2 \sin \pi/3 I_4(x_{02}) + I_4(x_{03})]. \quad (\text{A3-28})$$

Before evaluating the second term in (22) we must recall the SKLAR approximation²⁸ for three-center integrals:

$$(p^0 : rt) \approx (r | t) (p^0 : \bar{r}\bar{r}), \quad (\text{A3-29})$$

where r^0 is a point midway between the *equilibrium* positions of r^0 and t^0 and $(r | t)$ is the overlap of the displaced wave function Φ_r and Φ_t . Thus by (29) we may write the integral $(p^0 : rt)'$ as

$$(p^0 : rt)' \approx (r | t)' (p^0 : r^0 r^0) + (r^0 | t^0) (p^0 : \bar{r}\bar{r})'. \quad (\text{A3-30})$$

Defining $I_6(\bar{x}_{rp})$ as

$$I_6(\bar{x}_{rp}) = (p^0 : r^0 r^0) = - \int \Phi_r^0 \bar{\Psi}_{e-n}^{(p)0} \Phi_r^0 d\tau_{el}. \quad (\text{A3-31})$$

and recalling the expression for $(r | t)'$ (see A2-8, 9 and 10)

$$(r | t)' = -I_3(x_{rt}) [R_r \cos(\xi_{rt}, \Re_r) + Y_r \cos(\xi_{rt}, \Im_r) + R_t \cos(\xi_{tr}, \Re_t) + Y_t \cos(\xi_{tr}, \Im_t)] \quad (\text{A3-32})$$

we can derive

$$(r | t)' (p^0 : r^0 r^0) = -I_3(x_{rt}) I_6(\bar{x}_{rp}) [(R_r + R_t) \cos(\xi_{rt}, \Re_r) + (Y_r - Y_t) \cos(\xi_{rt}, \Im_r)]. \quad (\text{A3-33})$$

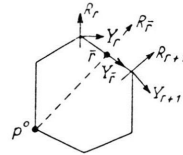
In analogy with equation (27) we have the second term of (30) as

$$(r^0 | t^0) (p^0 : \bar{r}\bar{r})' = -2 I_2(\bar{x}_{rt}) I_4(\bar{x}_{rp}) [R_{\bar{r}} \cos(\xi_{\bar{r}p}, \Re_{\bar{r}}) + Y_{\bar{r}} \cos(\xi_{\bar{r}p}, \Im_{\bar{r}})]. \quad (\text{A3-34})$$

But since the vectorial displacement of the midpoint r between atoms r and t is described by $\mathbf{s}_{\bar{r}} = \frac{1}{2}(\mathbf{s}_r + \mathbf{s}_t)$, we can write the components of $\mathbf{s}_{\bar{r}}$ (that is, $R_{\bar{r}}$ and $Y_{\bar{r}}$) in terms of R_l and Y_l , ($l=r, t$), by taking components of \mathbf{s}_r and \mathbf{s}_t along $\xi_{\bar{r}p}$ and perpendicular to $\xi_{\bar{r}p}$. For example, consider the terms $(r^0 | r^0 + 1) (p^0 : r r)'$. We see from the geometry pictured in Fig. 4, that $R_{\bar{r}}$ and $Y_{\bar{r}}$ are given by

$$\begin{aligned} R_{\bar{r}} &= \frac{1}{2} [\sin \pi/3 (R_r + R_{r+1}) + \cos \pi/3 (Y_r - Y_{r+1})], \\ Y_{\bar{r}} &= \frac{1}{2} [\cos \pi/3 (R_{r+1} - R_r) + \sin \pi/3 (Y_r + Y_{r+1})]. \end{aligned} \quad (\text{A3-35})$$

Fig. 4. Coordinate System for the Determination of $R_{\bar{r}}$ and $Y_{\bar{r}}$.



Hence, $(r^0 | r^0 + 1) (p^0 : r r)'$ is equal to

$$(r^0 | r^0 + 1) (p^0 : r r)' = -I_2(x_{01}) I_4(\bar{x}_{rp}) \begin{bmatrix} \sin \pi/3 (R_r + R_{r+1}) \cos(\xi_{\bar{r}p}, \Re_{\bar{r}}) \\ \cos \pi/3 (Y_r - Y_{r+1}) \cos(\xi_{\bar{r}p}, \Re_{\bar{r}}) \\ + \cos \pi/3 (R_{r+1} - R_r) \cos(\xi_{\bar{r}p}, \Im_{\bar{r}}) \\ + \sin \pi/3 (Y_r + Y_{r+1}) \cos(\xi_{\bar{r}p}, \Im_{\bar{r}}) \end{bmatrix}. \quad (\text{A3-36})$$

Now using the notation of Appendix I in evaluating the angles $\cos(\xi_{rp}, \Re_r)$ and $\cos(\xi_{rp}, \Im_r)$ we can derive the second term of (22) by the substitution of (33) and (34) into this term:

$$\sum_{r \neq t} (\omega^2)^{r+t} \sum_{\substack{p \neq r \\ p \neq t}} (p^0:rt)' = 6^{1/2} \mathcal{R}_{-2} \left[\begin{aligned} & 8 I_3(\bar{x}_{03}) I_6(\bar{x}_{01}) - 2 \sin \pi/3 I_3(\bar{x}_{02}) [I_6(1/2 \bar{x}_{01}) + 2 I_6((7/4)^{1/2} \bar{x}_{01}) + I_6(3/2 \bar{x}_{01})] \\ & - 2 I_3(\bar{x}_{01}) [I_6((7/4)^{1/2} \bar{x}_{01}) + I_6((13/4)^{1/2} \bar{x}_{01})] \\ & - 4 \sin \pi/3 I_2(\bar{x}_{01}) [\sin \omega_1 I_4((7/4)^{1/2} \bar{x}_{01}) + \cos \omega_4 I_4((13/4)^{1/2} \bar{x}_{01})] \\ & - I_2(\bar{x}_{02}) [I_4(3/2 \bar{x}_{01}) - I_4(1/2 \bar{x}_{01}) + 2 \cos \omega_1 I_4((7/4)^{1/2} \bar{x}_{01})] \end{aligned} \right] \\ + 2i 6^{1/2} \sin \pi/3 \mathcal{Y}_{-2} \left[\begin{aligned} & I_3(\bar{x}_{02}) [I_6(1/2 \bar{x}_{01}) + 2 I_6((7/4)^{1/2} \bar{x}_{01}) + I_6(3/2 \bar{x}_{01})] \\ & - 4 \sin \pi/3 I_3(\bar{x}_{01}) [I_6((7/4)^{1/2} \bar{x}_{01}) + I_6((13/4)^{1/2} \bar{x}_{01})] \\ & + 2 I_2(\bar{x}_{01}) [\sin \omega_1 I_4((7/4)^{1/2} \bar{x}_{01}) + \cos \omega_4 I_4((13/4)^{1/2} \bar{x}_{01})] \\ & + 2 \sin \pi/3 I_2(\bar{x}_{02}) [I_4(1/2 \bar{x}_{01}) - I_4(3/2 \bar{x}_{01}) - 2 \cos \omega_1 I_4((7/4)^{1/2} \bar{x}_{01})] \end{aligned} \right]. \quad (\text{A3-37})$$

$$\text{If we define } I_5(\bar{x}_{rt}) \text{ as } I_5(\bar{x}_{rt}) = \int \Phi_r^0 \cos \alpha_r [Z/2 a_0 \bar{\mathcal{V}}_{e-n}^{(r)0}] \Phi_t^0 d\tau_{el}, \quad (\text{A3-38})$$

we may, by methods similar to those used above, write the integrals $(r^0:r't^0)$ as

$$(r^0:r't^0) = -I_5(\bar{x}_{rt}) [R_r \cos(\xi_{rt}, \Re_r) + Y_r \cos(\xi_{rt}, \Im_r)]. \quad (\text{A3-39})$$

The substitution of the appropriate angles into (39) then allows one to express the third term in (22) as

$$\sum_{r \neq t} (\omega^2)^{r+t} (r^0:r't^0) \quad (\text{A3-40}) \\ = -6^{1/2} \mathcal{R}_{-2} [\cos \pi/3 I_5(\bar{x}_{01}) + \sin \pi/3 I_5(\bar{x}_{02}) - I_5(\bar{x}_{03})] + 2i \sin \pi/3 (6)^{1/2} \mathcal{Y}_{-2} [\cos \pi/3 I_5(\bar{x}_{02}) - \sin \pi/3 I_5(\bar{x}_{01})].$$

We finally obtain the desired formula for ε'_{-22} by substituting (23), (24), (28), (37) and (39) into (22):

$$\varepsilon'_{-22} = w_{2p}^0 S'_{-22} - 6^{1/2} \mathcal{R}_{-2} \left\{ \begin{aligned} & 1/6 (2 k_{01} \cos \pi/3 + 2 k_{02} \sin \pi/3 + k_{03}) \\ & + \sigma_2^2 \left[\begin{aligned} & 2 I_4(\bar{x}_{01}) + 4 \sin \pi/3 I_4(\bar{x}_{02}) + 2 I_4(\bar{x}_{03}) \\ & - 2 I_3(\bar{x}_{01}) [I_6((7/4)^{1/2} \bar{x}_{01}) + I_6((13/4)^{1/2} \bar{x}_{01})] \\ & - 2 \sin \pi/3 I_3(\bar{x}_{02}) [I_6(1/2 \bar{x}_{01}) + 2 I_6((7/4)^{1/2} \bar{x}_{01}) + I_6(3/2 \bar{x}_{01})] \\ & + 8 I_3(\bar{x}_{03}) I_6(\bar{x}_{01}) - I_5(\bar{x}_{01}) - 2 \sin \pi/3 I_5(\bar{x}_{02}) + 2 I_5(\bar{x}_{03}) \\ & - 4 \sin \pi/3 I_2(\bar{x}_{01}) [\sin \omega_1 I_4((7/4)^{1/2} \bar{x}_{01}) + \cos \omega_4 I_4((13/4)^{1/2} \bar{x}_{01})] \\ & - I_2(\bar{x}_{02}) [I_4(3/2 \bar{x}_{01}) - I_4(1/2 \bar{x}_{01}) + 2 \cos \omega_1 I_4((7/4)^{1/2} \bar{x}_{01})] \end{aligned} \right] \end{aligned} \right\} \\ - 2i \sigma_2^2 (6)^{1/2} \sin \pi/3 \mathcal{Y}_{-2} \left[\begin{aligned} & I_2(\bar{x}_{02}) [I_6(1/2 \bar{x}_{01}) + 2 I_6((7/4)^{1/2} \bar{x}_{01}) + I_6(3/2 \bar{x}_{01})] \\ & - 4 \sin \pi/3 I_3(\bar{x}_{01}) [I_6((7/4)^{1/2} \bar{x}_{01}) + I_6((13/4)^{1/2} \bar{x}_{01})] + I_5(\bar{x}_{02}) \\ & - 2 \sin \pi/3 I_5(\bar{x}_{01}) + 2 I_2(\bar{x}_{01}) [\sin \omega_1 I_4((7/4)^{1/2} \bar{x}_{01}) + \cos \omega_4 I_4((13/4)^{1/2} \bar{x}_{01})] \\ & + 2 \sin \pi/3 I_2(\bar{x}_{02}) [I_4(1/2 \bar{x}_{01}) - I_4(3/2 \bar{x}_{01}) - 2 \cos \omega_1 I_4((7/4)^{1/2} \bar{x}_{01})] \end{aligned} \right]. \quad (\text{A3-41})$$

A similar calculation performed for the term ε'_{1-1} yields

$$\varepsilon'_{1-1} = w_{2p}^0 S'_{1-1} - 6^{1/2} \mathcal{R}_{-2} \left\{ \begin{aligned} & 1/6 (2 k_{01} \cos \pi/3 + 2 k_{02} \sin \pi/3 + k_{03}) \\ & + \sigma_1^2 \left[\begin{aligned} & 2 I_4(\bar{x}_{01}) + 4 \sin \pi/3 I_4(\bar{x}_{02}) + 2 I_4(\bar{x}_{03}) - 8 I_3(\bar{x}_{03}) I_6(\bar{x}_{01}) \\ & - 2 \sin \pi/3 I_3(\bar{x}_{02}) [I_6(1/2 \bar{x}_{01}) + 2 I_6((7/4)^{1/2} \bar{x}_{01}) + I_6(3/2 \bar{x}_{01})] \\ & + 2 I_3(\bar{x}_{01}) [I_6((7/4)^{1/2} \bar{x}_{01}) + I_6((13/4)^{1/2} \bar{x}_{01})] \\ & + 4 \sin \pi/3 I_2(\bar{x}_{01}) [\sin \omega_1 I_4((7/4)^{1/2} \bar{x}_{01}) + \cos \omega_4 I_4((13/4)^{1/2} \bar{x}_{01})] \\ & - I_2(\bar{x}_{02}) [I_4(3/2 \bar{x}_{01}) - I_4(1/2 \bar{x}_{01}) + 2 \cos \omega_1 I_4((7/4)^{1/2} \bar{x}_{01})] \\ & + I_5(\bar{x}_{01}) - 2 \sin \pi/3 I_5(\bar{x}_{02}) - 2 I_5(\bar{x}_{03}) \end{aligned} \right] \end{aligned} \right\} \\ - 2i \sigma_1^2 (6)^{1/2} \sin \pi/3 \mathcal{Y}_{-2} \left[\begin{aligned} & I_3(\bar{x}_{02}) [I_6(1/2 \bar{x}_{01}) + 2 I_6((7/4)^{1/2} \bar{x}_{01}) + I_6(3/2 \bar{x}_{01})] \\ & + 4 \sin \pi/3 I_3(\bar{x}_{01}) [I_6((7/4)^{1/2} \bar{x}_{01}) + I_6((13/4)^{1/2} \bar{x}_{01})] \\ & - 2 I_2(\bar{x}_{01}) [\sin \omega_1 I_4((7/4)^{1/2} \bar{x}_{01}) + \cos \omega_4 I_4((13/4)^{1/2} \bar{x}_{01})] \\ & + 2 \sin \pi/3 I_2(\bar{x}_{02}) [I_4(1/2 \bar{x}_{01}) - I_4(3/2 \bar{x}_{01}) - 2 \cos \omega_1 I_4((7/4)^{1/2} \bar{x}_{01})] \\ & + I_5(\bar{x}_{02}) + 2 \sin \pi/3 I_5(\bar{x}_{01}) \end{aligned} \right]. \quad (\text{A3-42})$$

APPENDIX IV

Numerical Computation of the Integrals $I_j(\bar{x})$, ($j=0, 1, 2, 3, 4, 5, 6$), and the Constants k_{0j} , ($j=1, 2, 3$)

As the algebraic evaluation of the integrals $I_j(x)$ is quite involved²³, we shall defer a discussion of this topic for a future communication³¹. In this appendix we wish only to tabulate the numerical values which have been

| \bar{x} | $1/2 \bar{x}_{01}$ | $\bar{x}_{01} = 8.5$ | $(7/4)^{1/2} \bar{x}_{01}$ | $3/2 \bar{x}_{01}$ | $\bar{x}_{02} = (3)^{1/2} \bar{x}_{01}$ | $(13/14)^{1/2} \bar{x}_{01}$ | $x_{03} = 2 \bar{x}_{01}$ |
|-----------|--------------------|----------------------|----------------------------|--------------------|---|------------------------------|---------------------------|
| I_0 | 5.57652 | 1.49221 | 0.730917 | 0.549199 | 0.409108 | 0.378620 | 0.311261 |
| I_1 | — | 0.823900 | — | — | 0.062257 | — | 0.027965 |
| I_2 | — | 25.0946 | — | — | 3.59832 | — | 1.61435 |
| I_3 | — | — 13.6654 | — | — | — 2.47194 | — | — 1.16163 |
| I_4 | — 2.07558 | — 0.281089 | — 0.0520879 | — 0.0190637 | — 0.0047838 | — 0.0030994 | — 0.0008995 |
| I_5 | — | — 0.352045 | — | — | — 0.0208325 | — | — 0.0070083 |
| I_6 | 9.19373 | 0.912044 | 0.153300 | 0.053975 | — | 0.00833802 | — |
| k | — | — 0.943316 | — | — | — 0.382511 | — | — 0.298125 |

Tab. 4. Numerical Values of the Integrals $I_j(\bar{x})$, ($j=0, 1, \dots, 6$) and of the Constants k_{0j} [i. e., $k(\bar{x}_{0j})$]. The Integrals I_0 , I_1 , I_4 and I_5 and the Constants k_{0j} are measured in Units of $Z^2 e^2/a_0^2 \cdot 10^{-2}$. The Integrals I_2 , I_3 and I_6 are measured in Units of 10^{-2} , $Z/2 a_0 \cdot 10^{-2}$, and $Z e^2/a_0 \cdot 10^{-2}$, respectively.

obtained for these integrals as well as the numerical values of the constants k_{0j} , defined in equation (A 3—11) (see Table 4). For the sake of completeness we also report here the numerical values of the molecular orbital normalization factors σ_j^2 ($j = \pm 1, \pm 2$):

$$\sigma_1^2 = \sigma_{-1}^2 = 0.139026, \quad (\text{A4—1})$$

$$\sigma_2^2 = \sigma_{-2}^2 = 0.228557. \quad (\text{A4—2})$$

The numerical values for integrals γ_{ij}^0 , δ_{ij}^0 , ξ^0 , and η^0 were taken from the tabulation of PARR, CRAIG and ROSS¹⁸. The integrals $\varepsilon_j^0 - w_{2p}^0$, although not tabulated explicitly by PARR, CRAIG and ROSS¹⁸, are easily computed from the integrals which they have tabulated:

$$\begin{aligned} \varepsilon_0^0 - w_{2p}^0 &= -40.2560 \text{ e. v.} & \varepsilon_1^0 - w_{2p}^0 &= -37.3238 \text{ e. v.} \\ \varepsilon_2^0 - w_{2p}^0 &= -31.9655 \text{ e. v.} & \varepsilon_3^0 - w_{2p}^0 &= -29.2120 \text{ e. v.} \end{aligned} \quad (\text{A4—3})$$

³¹ A. D. LIEHR, Z. Naturforschg. **13a** [1958], in press.