Theory of Rydberg Series in Molecular Spectra

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In this note a method for calculating term values for molecular Rydberg series is given. The formulae thus derived are applied to a calculation of the benzene and ethylene term values.

Before considering the appearance of Rydberg series in molecular spectra, it is necessary to recall a few facts concerning atomic spectra. We first recall that a Rydberg series of spectral lines arises from an electron moving in an attractive electric field which, to good approximation, can be considered as coulombic. If the field were truly coulombic, as in the hydrogen atom, we would obtain the spectral term values, T_n, as

$$T_n = \frac{Z^2 R}{n^2}, \qquad (1)$$

$n = 1, 2, 3, \ldots, \infty$; $Z = 1$ for H; 2 for He II, 3 for Li III, etc.

Deviations from a coulombic potential manifest themselves in atomic spectra in two ways: (a) the appearance of non-integers in the denominator of equation (1); (b) the appearance of non-integral values of the nuclear charge Z. Thus alkali and X-ray spectral term values are written as

$$T_n = \frac{Z_{\text{eff}}^2 R}{n^{*2}}, \quad n^* = n - s; \quad n = 1, 2, 3, \ldots, \infty. \qquad (2)$$

The quantity s is called the quantum defect and the quantity Z_{eff} is called the effective nuclear charge. In atomic spectra the quantum defects and effective nuclear charges are calculated on the basis of penetrating hydrogen orbits and atomic core polarization effects [1, 2].

Now one would expect that when an electron in a polyatomic molecule is sufficiently excited, the net electric field acting upon it would be essentially coulombic. Hence, one would expect series of spectral lines in the far ultraviolet which obey the Ritz combination principle, the term values being given by (2). This is indeed seen experimentally. Furthermore, one would anticipate being able to compute, by means of perturbation theory, the term values for these Rydberg series. That this anticipation is justified will be shown below.

Theory

To facilitate our calculations, we assume that the net charge of a molecular ion is distributed over the molecule according to the electronegativities of the constituent atoms directly involved in the ionization process: for example, the removal of a π-electron in benzene would leave a uniformly charged ring of carbon atoms, a charge of $+e/6$ at each atom. Hence, we can write the Hamiltonian of a molecular ion plus planetary electrons as

$$\mathcal{H} = \mathcal{H}_{\text{molecular ion}} + \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - \sum_a \frac{z_a e^2}{|\vec{r_a}|} \qquad (3)$$

where $|\vec{r_a}|$ is the distance from atom a to the planetary electron, p_t^2 $(t = x, y, z)$ is the square of the momentum of the planetary electron, and z_a is the net ionic charge associated with atom a. The Hamiltonian, as written in equation (3), neglects exchange effects insofar as they concern the orbital electron.

We shall assume our unperturbed problem to be that of the planetary electron at infinity, moving in a hydrogenic orbital about the molecular ion. Thus

$$\mathcal{H}_0 = \mathcal{H}_{\text{molecular ion}} + \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) - \frac{q e^2}{|\vec{r}|} \qquad (4)$$

where q is the degree of ionicity of the molecule and $|\vec{r}|$ is the distance measured from the centroid of charge of the molecular ion to the hydrogenic

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[1] L. Pauling and S. Goudsmit, The Structure of Line Spectra, McGraw-Hill, New York 1930.

[2] H. White, Introduction to Atomic Spectra, McGraw-Hill, New York 1934.

electron. The unperturbed wave function can thus be written as

$$\Psi_0 = \mathcal{A}(1,2,\ldots,n)\{\Theta(1,2,\ldots,n-1)\ \Phi_{\mathrm{H}}(n)\}, \tag{5}$$

$\Theta(1,2,\ldots,n-1)$ being the wave function of the isolated ion core, $\Phi_{\mathrm{H}}(n)$ the hydrogenic orbital, and $\mathcal{A}(1,2,\ldots,n)$ the appropriate antisymmetrizing operator. Hence, once we have decomposed the complete Hamiltonian, $\mathcal{H}$, as given in (3), into an unperturbed part, $\mathcal{H}_0$, as given in (4), and a perturbation, $\mathcal{H}'$, we can determine the first order energy correction to $\mathcal{H}_0$ by the well-known quantum-mechanical formula

$$E' = \int \Psi_0^*\, \mathcal{H}'\, \Psi_0\, \mathrm{d}\tau, \tag{6}$$

Ψ_0 as in equation (5).

We can effect the desired decomposition of (3) by use of the multipole expansion [3] of $1/|\vec{r_a}|$. Now

$$\frac{1}{|\vec{r_a}|} = \frac{1}{|\vec{r}-\vec{x_a}|} = (r^2 + x_a^2 - 2\,r\,x_a\cos\lambda_a)^{-1/2}$$

$$= \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\cos\lambda_a)\,. \tag{7}$$

In equation (7) $\vec{x_a}$ is the distance from the centroid of ionic charge to atom a, λ_a is the angle between $\vec{r}$ and $\vec{x_a}$; and $r_>$ ist the maximum of r and x_a, $r_<$ the minimum: $\vec{r}$ and $\vec{r_a}$ are as defined in equations (3) and (4), respectively. Hence

$$\frac{1}{|\vec{r_a}|} = \frac{1}{r} + \frac{1}{r_>}\left[\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\cos\lambda_a) - \frac{r_>}{r}\right]. \tag{8}$$

Inserting (8) in (3), we have

$$\mathcal{H} = \mathcal{H}_{\text{molecular ion}} + \frac{1}{2\,m}(p_x^2 + p_y^2 + p_z^2) - \frac{e^2}{r}\sum_a z_a$$

$$- \frac{e^2}{r_>}\sum_a z_a\left[\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\cos\lambda_a) - \frac{r_>}{r}\right]. \tag{9}$$

Since Σz_a is equal to q, the degree of ionicity of the molecular core, we can write, on using (4)

$$\mathcal{H}' = -\frac{e^2}{r_>}\sum_a z_a\left[\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\cos\lambda_a) - \frac{r_>}{r}\right]. \tag{10}$$

[3] W. Magnus and F. Oberhettinger, Formulae and Theorems for the Functions of Mathematical Physics, Chelsea, New York 1954.

The substitution of (10) into equation (6) yields the correction to the hydrogenic energy levels due to the skeletal charge distribution:

$$E = E_0 + E' = E_{\text{core}} - \frac{R\,h\,c}{n^2} + E'. \tag{11}$$

The desired term values for the molecule are then obtained from equation (11) as

$$T_n = \frac{R}{n^2} - \frac{E'}{h\,c}. \tag{12}$$

Application to Benzene

We shall in this section be concerned with the calculation of the term values, T_n, for the benzene molecule with one electron in an np hydrogen orbital. The appropriate zero-order functions $\Psi_0^{(j)}$ $(j=1,2)$ are:

$$\Psi_0^{(1)} = (2)^{-1/2}\,(6\,!)^{-1/2}\,[|\,\psi_0(1)\,\bar{\psi}_0(2)\,\psi_1(3)\,\bar{\psi}_1(4)\,\psi_{-1}(5)\,\overline{\mathrm{np}}(6)| - |\,\psi_0(1)\,\bar{\psi}_0(2)\,\psi_1(3)\,\bar{\psi}_1(4)\,\bar{\psi}_{-1}(5)\,\mathrm{np}(6)|],$$

$$\Psi_0^{(2)} = (2)^{-1/2}\,(6\,!)^{-1/2}\,[|\,\psi_0(1)\,\bar{\psi}_0(2)\,\psi_{-1}(3)\,\bar{\psi}_{-1}(4)\,\psi_1(5)\,\overline{\mathrm{np}}(6)| - |\,\psi_0(1)\,\bar{\psi}_0(2)\,\psi_{-1}(3)\,\bar{\psi}_{-1}(4)\,\bar{\psi}_1(5)\,\mathrm{np}(6)|], \tag{13}$$

the $\psi_l(l=0,\pm1)$ being the benzene molecular orbitals. Now since by spin and orbit orthogonality

$$\int \Psi_0^{(1)*}\,\mathcal{H}'\,\Psi_0^{(2)}\,\mathrm{d}\tau = 0\,, \tag{14}$$

the degeneracy of $\Psi_0^{(j)}$ $(j=1,2)$ is not lifted by the np electron peneration. Hence, we can, for our calculations, use either function. We shall choose to use $\Psi_0^{(1)}$ in the following computations.

Now we have the relation

$$E' = \int \Psi_0^{(1)*}\,\mathcal{H}'\,\Psi_0^{(1)} = \int \mathrm{np}\,\mathcal{H}'\,\mathrm{np} - \tfrac{1}{3}\left(\int \psi_0\,\mathrm{np}\,\mathrm{d}\tau\right)\left(\int \psi_0\,\mathcal{H}'\,\mathrm{np}\,\mathrm{d}\tau\right). \tag{15}$$

If the z-axis is chosen perpendicular to the benzene ring, we have ψ_0 is orthogonal to np_x and np_y by symmetry, so that

$$E'_{x,y} = \int \mathrm{np}_{x,y}\,\mathcal{H}'\,\mathrm{np}_{x,y}\,\mathrm{d}\tau\,. \tag{16}$$

However, np_z is not orthogonal to ψ_0. But in the region of high principal quantum number n, their overlap will be small, so that the last term in (15) will be negligible in comparison with the first. Then

we can write

$$E'_z = \int \mathrm{np}_z \, \mathcal{H}' \, \mathrm{np}_z \, \mathrm{d}\tau \,. \tag{17}$$

If $|\vec{x_a}| = x$ is the distance from the center of the benzene ring to any carbon atom we have (10) as (taking $z_a = 1/6$, all a)

$$\mathcal{H}' = -\frac{e^2}{6x}\left[\sum_{l=0}^{\infty}\left(\frac{r}{x}\right)^l \sum_{a=0}^{5} P_l(\cos\lambda_a) - \frac{6x}{r}\right], \quad x > r \,;$$

$$\mathcal{H}' = -\frac{e^2}{6r}\left[\sum_{l=0}^{\infty}\left(\frac{x}{r}\right)^l \sum_{a=0}^{5} P_l(\cos\lambda_a) - 6\right], \quad r > x \,. \tag{18}$$

Now

$$\cos\lambda_a = \cos\vartheta\cos\frac{\pi}{2} + \sin\vartheta\sin\frac{\pi}{2}\cos\left(\varphi - \frac{2\pi a}{6}\right). \tag{19}$$

Then by the addition theorem for LEGENDRE polynomials [3]

$$P_l(\cos\lambda_a) = \sum_{m=-l}^{+l} \frac{(l-m)!}{(l+m)!} P_l^m(\cos\vartheta)\, P_l^m\left(\cos\frac{\pi}{2}\right) e^{im\varphi}\, e^{-im2\pi a/6} \,. \tag{20}$$

Substituting (20) into (18) we have

$$\mathcal{H}' = -\frac{e^2}{6x}\left[\sum_{l=0}^{\infty}\left(\frac{r}{x}\right)^l \sum_{m=-l}^{+l} \frac{(l-m)!}{(l+m)!} P_l^m(\cos\vartheta)\, P_l^m\left(\cos\frac{\pi}{2}\right) e^{im\varphi} \sum_{a=0}^{5} (e^{-2\pi im/6})^a - \frac{6x}{r}\right], \quad x > r \,,$$

$$\mathcal{H}' = -\frac{e^2}{6r}\left[\sum_{l=0}^{\infty}\left(\frac{x}{r}\right)^l \sum_{m=-l}^{+l} \frac{(l-m)!}{(l+m)!} P_l^m(\cos\vartheta)\, P_l^m\left(\cos\frac{\pi}{2}\right) e^{im\varphi} \sum_{a=0}^{5} (e^{-2\pi im/6})^a - 6\right], \quad r > x \,. \tag{21}$$

Inspection of the appropriate ARGAND diagram shows that

$$\sum_{a=0}^{5} (e^{-2\pi im/6})^a = 6\,\delta_{m,6k} \quad (k = 0, 1, 2, \ldots, \infty) \,. \tag{22}$$

So

$$\mathcal{H}' = -\frac{e^2}{x}\left\{\sum_{l \geqq 6m}^{\infty} \sum_{6m=-l}^{+l} e^{6im\varphi} \left(\frac{r}{x}\right)^l P_l^{6m}(\cos\vartheta)\, P_l^{6m}\left(\cos\frac{\pi}{2}\right) - \frac{x}{r}\right\}, \quad x > r \,;$$

$$\mathcal{H}' = -\frac{e^2}{r}\left\{\sum_{l \geqq 6m}^{\infty} \sum_{6m=-l}^{+l} e^{6im\varphi} \left(\frac{x}{r}\right)^l P_l^{6m}(\cos\vartheta)\, P_l^{6m}\left(\cos\frac{\pi}{2}\right) - 1\right\}, \quad r > x \,. \tag{23}$$

Recalling that [4]

$$\mathrm{np}_x = \left(\frac{3}{4\pi}\right)^{1/2} c_{n1}\, R_{n1}(r)\, \sin\vartheta\cos\varphi \,;$$
$$\mathrm{np}_y = \left(\frac{3}{4\pi}\right)^{1/2} c_{n1}\, R_{n1}(r)\, \sin\vartheta\sin\varphi \,; \tag{24}$$
$$\mathrm{np}_z = \left(\frac{3}{4\pi}\right)^{1/2} c_{n1}\, R_{n1}(r)\, \cos\vartheta \,,$$

where $c_{n1}^2 \int_0^\infty R_{n1}^2(r)\, r^2\, \mathrm{d}r = 1$, we can write (16) and (17) as

$$E_x' = E_y' = \frac{3}{4\pi} c_{n1}^2 \int R_{n1}^2(r)\, \sin^2\vartheta\cos^2\varphi\, \mathcal{H}'\, \mathrm{d}\tau \,;$$
$$E_z' = \frac{3}{4\pi} c_{n1}^2 \int R_{n1}^2(r)\, \cos^2\vartheta\, \mathcal{H}'\, \mathrm{d}\tau \,. \tag{25}$$

Before substituting (23) into (25) a great simplification is introduced if one utilizes the substitutions [3]

$$\cos^2\vartheta = \tfrac{1}{3}[2P_2(\cos\vartheta) + P_0(\cos\vartheta)] \,;$$
$$\sin^2\vartheta = \tfrac{2}{3}[P_0(\cos\vartheta) - P_2(\cos\vartheta)] \,, \tag{26}$$

together with the relation [3]

$$\int_0^\pi P_l(\cos\vartheta)\, P_{l'}(\cos\vartheta)\, \sin\vartheta\, \mathrm{d}\vartheta = \frac{2}{2l+1}\delta_{l,l'} \,. \tag{27}$$

[4] L. PAULING and E. B. WILSON, Jr., Introduction to Quantum Mechanics, McGraw-Hill, New York 1935.

If we now use (26) and (27) in (25) we have

$$E_x' = E_y' = -e^2 c_{n1}^2 \left[\int_0^x R_{n1}^2(r) \left[\frac{1}{x} - \frac{1}{r}\right] r^2 \, dr + \frac{1}{10\, x^3} \int_0^x R_{n1}^2(r)\, r^4 \, dr + \frac{x^2}{10} \int_x^\infty R_{n1}^2(r) \frac{dr}{r} \right];$$

$$E_z' = -e^2 c_{n1}^2 \left[\int_0^x R_{n1}^2(r) \left[\frac{1}{x} - \frac{1}{r}\right] r^2 \, dr - \frac{1}{5\, x^3} \int_0^x R_{n1}^2(r)\, r^4 \, dr - \frac{x^2}{5} \int_x^\infty R_{n1}^2(r) \frac{dr}{r} \right]. \tag{28}$$

Using the algebraic forms given in reference [4] for the functions $R_{n1}(r)$ in (28), we obtain the numerical results given in Table 1. Also tabulated in Table 1 are the term values assigned by PRICE and WOOD [5] to the two strong RYDBERG series which converge to the same limit in the far ultra-violet spectrum of benzene.

n	T_{nz}	$T_{nx}=T_{ny}$	$R/(n+0.55)^2$	$R/(n-0.03)^2$
2	18,602 cm^{-1}	25,522 cm^{-1}	16,867 cm^{-1}	28,261 cm^{-1}
3	9,744	11,378	8,703	12,434
4	5,849	6,481	5,298	6,959
5	3,878	4,188	3,561	4,440
6	2,782	2,905	2,556	3,077

Table 1.

In a recent letter to the editor [6], MOFFITT and the author have proposed that the observed RYDBERG spectrum of benzene arises from a $\psi_{e_{1g}} \rightarrow$ np transition. It is thus gratifying that our simple model of the np RYDBERG state of benzene yields calculated term values in good agreement with experiment [7].

Application to Ethylene

In this section we shall be concerned with the calculation of the term values, T_n, for an ethylene molecule having one electron in a np hydrogen orbital. The appropriate zero-order wave function, Ψ_0, is thus given by

$$\Psi_0 = \tfrac{1}{2}\{|\psi_+(1)\,\overline{\mathrm{np}}(2)| - |\psi_+(1)\,\mathrm{np}(2)|\}, \tag{29}$$

where ψ_+ is the normalized b_{2u} molecular orbital of ethylene. Substituting (29) in equation (6) yields

$$E' = \int \mathrm{np}\, \mathcal{H}'\, \mathrm{np}\, d\tau + \int \psi_+\, \mathrm{np}\, d\tau \cdot \int \psi_+\, \mathcal{H}'\, \mathrm{np}\, d\tau . \tag{30}$$

If we choose the z-axis in ethylene to be along the carbon – carbon bond, we have that ψ_+ and $\mathrm{np}_{z,y}$ are orthogonal. Hence

$$E'_{y,z} + \int \mathrm{np}_{y,z}\, \mathcal{H}'\, \mathrm{np}_{y,z}\, d\tau . \tag{31}$$

Unfortunately, ψ_+ is not orthogonal to np_x. However, in the region of high principal quantum number n, their overlap will be small, so that the last term in (30) will become negligible in comparison with the first. Thus we can also write

$$E_x' = \int \mathrm{np}_x\, \mathcal{H}'\, \mathrm{np}_x\, d\tau . \tag{32}$$

If $2x$ is the carbon – carbon bond distance in the ethylene plus one ion, we can write the perturbation term given in equation (10) as (taking $z_1 = z_2 = 1/2$)

$$\mathcal{H}' = -\frac{e^2}{2x}\left\{ \sum_{l=0}^{\infty} \left(\frac{r}{x}\right)^l P_l(\cos\vartheta) + P_l(\cos(\pi - \vartheta)) - \frac{2x}{r} \right\}, \quad x > r ;$$

$$\mathcal{H}' = -\frac{e^2}{2r}\left\{ \sum_{l=0}^{\infty} \left(\frac{x}{r}\right)^l P_l(\cos\vartheta) + P_l(\cos(\pi - \vartheta)) - 2 \right\}, \quad r > x . \tag{33}$$

[5] W. C. PRICE and R. W. WOOD, J. Chem. Phys. **3**, 439 [1935].

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

[7] Recently P. G. WILKINSON has re-investigated the vacuum ultraviolet spectrum of benzene. His data are in good agreement with those of PRICE and WOOD [5]. See Canad. J. Phys. **34**, 596 [1956].

Since $P_l(-y) = (-1)^l P_l(y)$, equation (33) simplifies to

$$\mathcal{H}' = -\frac{e^2}{2x}\left\{2\sum_{l=0}^{\infty}\left(\frac{r}{x}\right)^{2l} P_{2l}(\cos\vartheta) - \frac{2x}{r}\right\}, \quad x > r\,;$$
$$\mathcal{H}' = -\frac{e^2}{2r}\left\{2\sum_{l=0}^{\infty}\left(\frac{x}{r}\right)^{2l} P_{2l}(\cos\vartheta) - 2\right\}, \quad r > x\,. \tag{34}$$

Substituting the relations contained in equations (24), (26), (27), and (34) into equations (31) and (32), we obtain the desired energies

$$E_x' = E_y' = -e^2 c_{n1}^2\left\{\int_0^x R_{n1}^2(r)\left[\frac{1}{x}-\frac{1}{r}\right]r^2\,\mathrm{d}r - \frac{1}{5x^3}\int_0^x R_{n1}^2(r)\,r^4\,\mathrm{d}r - \frac{x^2}{5}\int_x^{\infty} R_{n1}^2(r)\,\frac{\mathrm{d}r}{r}\right\},$$
$$E_z' = -e^2 c_{n1}^2\left\{\int_0^x R_{n1}^2(r)\left[\frac{1}{x}-\frac{1}{r}\right]r^2\,\mathrm{d}r + \frac{2}{5x^3}\int_0^x R_{n1}^2(r)\,r^4\,\mathrm{d}r + \frac{2x^2}{5}\int_x^{\infty} R_{n1}^2(r)\,\frac{\mathrm{d}r}{r}\right\}. \tag{35}$$

If we use the algebraic forms given in reference [4] for the functions $R_{n1}(r)$ of equation (35), we obtain the numerical results presented in Table 2.

PRICE and TUTTE [8], and more recently WILKINSON and MULLIKEN [9], have found in the far ultraviolet spectrum of ethylene two weak RYDBERG series converging to the same limit, in addition to the strong $\psi_{b_{2u}} \rightarrow$ ns RYDBERG progression. These two weak series, tabulated in Table 2, were fitted by PRICE and TUTTE to the term values $R/(n+0.4)^2$ and $R/(n-0.3)^2$. We shall give a plausible argument for the assignment of these lines to the $\psi_{b_{2u}} \rightarrow$ np transition, in which the np RYDBERG state of ethylene is in the perpendicular form (D_{2d}).

n	T_{nz}	$T_{nx}=T_{ny}$	$T_n=R/(n+0.4)^2$	$T_n=R/(n-0.3)^2$
2	31,290 cm^{-1}	24,590 cm^{-1}	19,041 cm^{-1}	37,951 cm^{-1}
3	13,211	11,367	9,488	15,045
4	7,269	6,512	5,665	8,012
5	4,600	4,210	3,761	4,965
6	3,171	2,943	2,678	3,376

Table 2.

If we assume the RYDBERG state of ethylene possesses the symmetry D_{2h}, we would expect to see at least one of the transitions $\psi_{b_{2u}} \rightarrow$ ns, or nd, or ng, etc. On the other hand, if we assume this state has symmetry D_{2d} (or lower), we would expect to see at least one of the transitions $\psi_{b_{2u}} \rightarrow$ ns, or np, or nd, or nf, etc. Now because of the *approximate axial symmetry* of both the D_{2h} and D_{2d} RYDBERG states, we conclude that each of the degenerate hydrogenic levels is split into the following number of components: the np state possesses two components, the nd three, the nf four, ng five, etc. It is readily verified that all of these components are optically allowed for a potential field of symmetry D_{2d} or lower. For a potential field of symmetry D_{2h}, one may easily show that all of the distinct components of the even angular momentum hydrogenic states are optically allowed. Hence, the only consistent assignment for the RYDBERG series of ethylene is $\psi_{b_{2u}} \rightarrow$ ns + np. As the $\psi_{b_{2u}} \rightarrow$ np transition is formally forbidden for planar ethylene (D_{2h}), but allowed for perpendicular ethylene (D_{2d}), we conclude that ethylene is of the perpendicular configuration in its np RYDBERG state [10]. As both planar and perpendicular forms of the ethylene RYDBERG state yield an allowed $\psi_{b_{2u}} \rightarrow$ ns transition, the preceding arguments yield no information as to the configuration of the ns state [11]. Since both our qualitative and quantitative (see Table 2) considerations agree with the experimental findings, we may

[8] W. C. PRICE and W. T. TUTTE, Proc. Roy. Soc., Lond. A, **174**, 207 [1940].

[9] P. G. WILKINSON and R. S. MULLIKEN, J. Chem. Phys. **23**, 1895 [1955].

[10] Vibronic perturbations of a D_{2h} RYDBERG state also account for the appearance of the np hydrogenic levels. However, the author feels that this mechanism is less probable than the explanation given above. It is of course possible that the symmetry of the RYDBERG state is lower than D_{2h} or D_{2d}. However, as the RYDBERG level splittings depend, to a first approximation, only on the axial carbon atoms, the conclusions drawn above for D_{2d} symmetry hold equally well for the less symmetric configurations of ethylene.

[11] The theoretical considerations of MULLIKEN indicate a planar ns state. See reference [8] for further details.

assign the two weak RYDBERG progressions of PRICE and TUTTE as $(\psi_{b_{2u}})^2\,(D_{2h}) \rightarrow (\psi_e)\,np\,(D_{2d})$.

The results obtained for ethylene and benzene in this and the previous section are also applicable to the substituted ethylenes and benzenes, as the calculations outlined above depended only on the form of the carbon skeleton. However, only the qualitative results would be expected to be valid for these substituted compounds because of the resultant non-uniform charge distribution.

Note added in proof: Recently P. G. WILKINSON (Canad. J. Phys. **34**, 643 [1956]) has reinvestigated the vacuum ultraviolet spectrum of ethylene. He has found a fourth RYDBERG series having the same ionization limit as the $\psi_{b_{2u}} \rightarrow ns$ transition. Since the experimental term values, $T_n = R/(n+0.05)^2$, of this new RYDBERG progression agree closely with those computed for the $\psi_{b_{2u}} \rightarrow np_{x,y}$ transition, we assign this new series as $\psi_{b_{2u}} \rightarrow np_{x,y}$. This assignment implies that the ethylene RYDBERG state is of a lower symmetry than D_{2d} .

NOTIZEN

Die Nukleonenverteilung in schweren Kernen *

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(Z. Naturforschg. **11 a**, 757—758 [1956]; eingegangen am 2. August 1956)

In einer früheren Arbeit [1] wurde gezeigt, daß eine relativ stärkere Anhäufung der Neutronen als der Protonen am Rand schwerer Kerne im wesentlichen dadurch zustande kommt, daß auf die Protonen am Kernrand eine stärkere rücktreibende Kraft (Asymmetriekraft) ausgeübt wird als auf die Neutronen. Diese Asymmetriekraft überwiegt bei weitem die COULOMBsche Abstoßungskraft der Protonen [1]. Die Verteilung der Neutronen und Protonen wurde dabei sehr roh abgeschätzt. Zum Beispiel wurde noch nicht berücksichtigt, daß das resultierende Protonenpotential, das für die Kraftwirkung auf ein einzelnes Proton maßgebend ist, wegen der elektrischen Ladung der Protonen vom Kerninnern zum Kernrand hin abfällt.

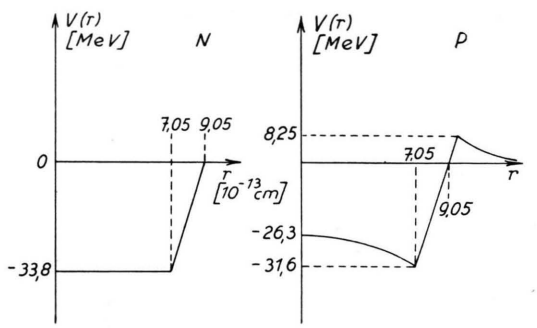

Abb. 1.

Mit Hilfe der Integrieranlage der Siemens-Schuckert-Werke in Erlangen wurde diese Dichteverteilung nun genauer berechnet. Insbesondere wurde das COULOMB-Potential der Protonen genauer berücksichtigt. Als Modellkern für die Berechnung der Dichteverteilung der Nukleonen wurde der Kern Yb^{176}_{70} genommen. Das resultierende Neutronen- bzw. Protonenpotential wurde wieder aus der WEIZSÄCKER-BETHE-Formel abgeleitet [1]. Die Abfallsbreite des Kernpotentials am Kernrand wurde wieder zu $2 \cdot 10^{-13}$ cm angenommen [1]. Zur Berechnung des COULOMB-Potentials im Kerninneren wurde eine gleichmäßige Verteilung der Protonen über den ganzen Kern angenommen. Die Protonen- und Neutronenpotentialtiefe wurde dabei so festgelegt, daß die Protonen bzw. Neutronen am oberen Rand der FERMI-Kugel eine Bindungsenergie von ungefähr 5 MeV besitzen. Es ergaben sich damit die beiden in Abb. 1 angegebenen Potentialformen.

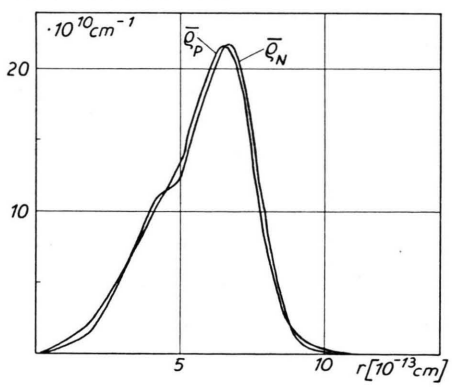

Abb. 2.

* Nach Fertigstellung dieser Notiz erschien eine Arbeit von ROSS, MARK und LAWSON über die Nukleonenverteilung in schweren Kernen (unter Berücksichtigung der Spin-Bahn-Kopplung) [4]. Hierbei wurden als Nukleonenpotentiale Potentiale der Form $V(r) = -V_0/(1+e^{a(r-a)})$ genommen. Die dort gebrachten Ergebnisse stimmen mit unseren Ergebnissen in ihrem allgemeinen Verhalten gut überein.

[1] K. WILDERMUTH, Z. Naturforschg. **9 a**, 1047 [1954]. — Siehe auch: M. H. JOHNSON u. E. TELLER, Phys. Rev. **93**, 357 [1954]. — P. MITTELSTAEDT, Z. Naturforschg. **10 a**, 379 [1955]. — W. WILD, Bayer. Akad. Wiss., Math.-Naturwiss. Klasse **18**, 371 [1956].