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On the Coupling Between Electronic and Nuclear Motions in Molecules

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The energy due to the coupling between the electronic and the nuclear motion in a molecular system has been calculated for the normal state of the hydrogen molecular ion H_2^+ and the lowest $^1\Sigma$ and $^3\Sigma$ state of the hydrogen molecule H_2 . It is found that this coupling is represented by a repulsive potential which is of the same order of magnitude as the van der Waals interactions at distances where the latter is important. Thus in any theoretical calculation of the interaction between light neutral atoms, it is necessary to include this coupling between the electronic and the nuclear motions.

INTRODUCTION

IT is well known that in the usual treatment of the energy of a molecular system in which the Schrödinger equation is first solved for fixed nuclear configurations and the electronic energy so obtained is regarded as the effective potential for the nuclear motion, the coupling between the electronic and the nuclear motion is neglected. This coupling energy, being of the order of the ratio of the electronic and nuclear masses times the total energy, i.e., $\sim 10^{-4}$ ev, is small and is negligible in comparison with the electronic energies. However, when one is interested in such problems as the interaction between two neutral atoms (for example, two helium atoms in their ground state, or the H_2 molecule in the repulsive $^3\Sigma$ state), one deals with the very small interactions known as van der Waals interactions. These interactions, calculated either by treating the interaction between the induced dipoles of the two atoms as perturbations, or by including the electron-electron correlation in the wave function by using wave functions of the Hylleraas-James-Coolidge type, give rise to a weak attraction at large interatomic distances, with a minimum in the potential of the order 10^{-16} erg/mole. These energies are now just of the same order of magnitude as the coupling between the electronic and the nuclear motion. Thus it seems that in any treatment of the van der Waals interaction, it is not justified to neglect the effect of the electron-nuclear coupling without having an estimate of it made. The purpose of the present note is to make such an estimate for the lowest electronic states of the molecules H_2^+ and H_2 .

THEORY AND CALCULATIONS

The theory of the electronic and nuclear motion of a molecular system is well known from the early work of Born and Oppenheimer.¹ In that theory, which is valid for nuclear motions about stable configurations, the lowest order approximation in the series expansion in powers of $(m/M)^{1/2}$ (or, rather, in powers of the normal coordinates of the vibrational motions) is the familiar static-nuclei approximation. The electronic energy of the molecule is first calculated for *fixed* configurations

of the nuclei, and this energy, containing the nuclear coordinates as parameters, is the "potential" for the nuclear vibrations. The coupling between the electronic and the nuclear motions is represented in the higher approximations. No calculations have been made for an actual molecule, probably because the theory involving the expansion in powers of $(m/M)^{1/2}$ is not in a convenient form for such calculations and the general order of magnitude of this coupling is known to be negligibly small in all the usual considerations of the electronic energy of molecules. More recently the theory of molecular energy has been given by Born² in an exact form which does not depend on such an expansion and whose validity is hence not restricted to nuclear motions about configurations of stable equilibrium. Thus it is particularly suitable for the calculation of the effect of this coupling for the repulsive states between neutral atoms for which the van der Waals interactions have been considered important at large distances.

Let the electronic and nuclear coordinates and masses be collectively denoted by $x, m; X, M$, respectively. The Hamiltonian of the molecular system is:

$$H = -\frac{\hbar^2}{2m}\Delta_x - \frac{\hbar^2}{2M}\Delta_X + U(x, X),$$

summation over all electrons and nuclei being implied. Let the problem for fixed nuclei be assumed to have been solved, i.e.,

$$\left[-\frac{\hbar^2}{2m}\Delta_x + U(x, X) \right] \phi_n(x, X) = E_n \phi_n(x, X),$$

where the electronic wave function for state n is normalized for all values of the nuclear coordinates X appearing as parameters. The solution Ψ of

$$H\Psi(x, X) = E\Psi(x, X)$$

² M. Born, *Nachr. Akad. Wiss. Göttingen* 1, (1951); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Appendix 8; Also Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), pp. 925.

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¹ M. Born and J. R. Oppenheimer, *Ann. Physik* 84, 457 (1927).

is then expanded in series of the ϕ_n ,

$$\Psi(x, X) = \sum \psi_n(X) \phi_n(x, X).$$

It can then easily be shown that the $\psi_n(X)$ are given by the following system of differential integral equations:

$$\left[-\frac{\hbar^2}{2M} \Delta_X + V_n(X) - E \right] \psi_n(X) + \sum_k' C_{nk} \left(X, \frac{\partial}{\partial X} \right) \psi_k(X) = 0, \quad (1)$$

where

$$V_n(X) = E_n(X) + E_n^e(X),$$

$$E_n^e(X) = -\sum_i \frac{\hbar^2}{2M_i} \int \phi_n^*(x, X) \Delta_{X_i} \phi_n(x, X) dx, \quad (2)$$

and

$$C_{nk} = -\sum_i \frac{\hbar^2}{2M_i} \left(A_{nk}^{(i)}(X) \frac{\partial}{\partial X_i} + B_{nk}^{(i)}(X) \right),$$

$$A_{nk}^{(i)} = \int \phi_n^*(x, X) \frac{\partial}{\partial X_i} \phi_k(x, X) dx,$$

$$B_{nk}^{(i)} = \int \phi_n^*(x, X) \Delta_{X_i} \phi_k(x, X) dx.$$

The system of Eqs. (1) is exact. To solve (1) would, however, entail the knowledge of all the electronic states ϕ_k of the system. If in a first approximation, one neglects the nondiagonal matrix elements C_{nk} in (1) that represent the effect of other electronic states, Eq. (1) then reduces to

$$\left[-\frac{\hbar^2}{2M} \Delta_X + V_n(X) - E \right] \psi_n(X) = 0, \quad (3)$$

with $V_n(X)$ given by (2). There the second term represents the coupling between the electronic and the nuclear motion, and appears in the form of a correction to the usual potential $E_n(X)$ obtained in the static-nuclei approximation.

In the present note we shall apply the above theory to an approximate calculation of the coupling energy for the lowest state of H_2^+ and the lowest $^1\Sigma, ^3\Sigma$ states of H_2 . Since the effect being calculated is a small one, and since we shall only be able to use the approximation represented by (3), we shall employ for both molecules the simplest wave functions.

Hydrogen Molecular Ion H_2^+

For the ground state $1s\sigma\Sigma$, we shall use the wave function of Guillemin and Zener³

³ V. Guillemin and C. Zener, Proc. Natl. Acad. Sci. **15**, 314 (1929).

$$\Psi(\mathbf{r}, \mathbf{X}_A, \mathbf{X}_B) = N\psi$$

$$= N[\exp\{-\gamma(r_A + \delta r_B)/a\} + \exp\{-\gamma(r_B + \delta r_A)/a\}], \quad (4)$$

where r_A, r_B are the distances of the electron from the nuclei A and B , and N is the normalization factor which depends on \mathbf{X}_A and \mathbf{X}_B only through $|\mathbf{X}_A - \mathbf{X}_B|$. On transforming from the coordinates $\mathbf{X}_A, \mathbf{X}_B$ to the relative coordinate $\mathbf{R} = \mathbf{X}_A - \mathbf{X}_B$ and the center of mass (of the nuclei) coordinate $\Lambda = \frac{1}{2}(\mathbf{X}_A + \mathbf{X}_B)$ one has

$$\frac{1}{2}(\Delta_{X_A} + \Delta_{X_B}) = \frac{1}{4}\Delta_\Lambda + \Delta_R. \quad (5)$$

From the fact that $\Psi(\mathbf{r}, \mathbf{X}_A, \mathbf{X}_B)$ is normalized for all nuclear coordinates, and the fact that $N = N(R)$ does not depend on Λ , it can be easily shown that

$$\int \Psi(\frac{1}{4}\Delta_\Lambda + \Delta_R) \Psi d\tau = N^2 \int \psi(\frac{1}{4}\Delta_\Lambda + \Delta_R) \psi d\tau + \frac{1}{N} \Delta_R N - 2 \left(\frac{1}{N} \nabla_R N \right)^2. \quad (6)$$

It is important that, in the calculation of (6) with Ψ given by (4) or any other form, the differentiation in (6) be first carried out and the resulting expressions may then be transformed in terms of elliptic coordinates ξ, η for convenience in integration. Thus

$$R\xi = r_A + r_B, \quad R\eta = r_A - r_B,$$

$$\lambda a = R(\gamma + \delta) \equiv R\alpha, \quad \mu a = R(\gamma - \delta) \equiv R\beta,$$

$$\psi = \exp\left(-\frac{\lambda}{2}\xi\right) \left[\exp\left(\frac{\mu}{2}\eta\right) + \exp\left(-\frac{\mu}{2}\eta\right) \right], \quad (7)$$

$$d\tau = \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\varphi, \quad S = e^\mu + e^{-\mu}, \quad D = e^\mu - e^{-\mu},$$

$$Q = \frac{1}{2} \left(\frac{\alpha}{\beta} \right)^2 \left[S - \frac{D}{\mu} + \frac{\beta}{\alpha} \left(1 + \frac{\beta}{\alpha\mu} \right) D \right] + 1 + \lambda + \frac{\lambda^2}{3}.$$

It can be shown that $E^e(X)$ in (2), with (5), is given by

$$\begin{aligned} E^e(R) = & \frac{\hbar^2}{2Ma^2} \left[\frac{\alpha^2 + \beta^2}{2} - \frac{\beta^2}{Q} \left(1 + \lambda + \frac{\lambda^2}{3} \right) - \frac{\alpha^2}{18Q} \right. \\ & \times \left\{ \lambda + \lambda^2 + \frac{3}{2} \left(\frac{\alpha^2}{\beta^2} - 1 \right) \left(1 + \frac{\beta}{\alpha\mu} \right) \left(S - \frac{D}{\mu} \right) \right\}^2 \\ & + \frac{1}{\alpha^3} \frac{d^2\alpha}{d\rho^2} + \frac{6}{\alpha^2\lambda} \left\{ 1 + \frac{4(1+\lambda)\lambda^2}{9Q} + \frac{(1+\lambda)^2\lambda^2}{27Q^2} \right\} \frac{d\alpha}{d\rho} \\ & \left. + \frac{3}{\alpha^4} \left\{ 1 + \frac{2\lambda^4}{45Q} - \frac{(1+x)\lambda^4}{54Q^2} \right\} \left(\frac{d\alpha}{d\rho} \right)^2 \right], \quad (8) \end{aligned}$$

where $\rho = R/a$. In (8), the last few terms in $d\alpha/d\rho, d^2\alpha/d\rho^2$ have been obtained from the function (7) with

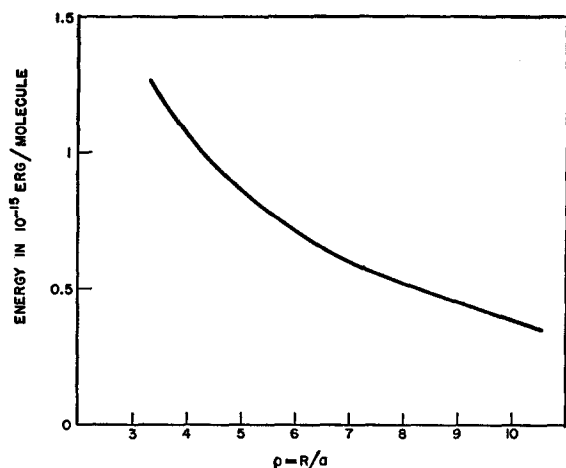


FIG. 1. Correction potential $E^c(R) - E^c(\infty)$, for the $1s\sigma$ state of H_2^+ , due to the coupling between the electronic and the nuclear motions. The abscissa is nuclear separations in units of the Bohr radius a .

$\alpha = \beta$ since these terms are small and their calculation with $\alpha \neq \beta$ is unduly lengthy.

It is interesting to note that the following asymptotic values of $E^c(R)$:

(1) $R \rightarrow \infty$. In this limit, $\alpha = \beta \rightarrow 1$ and

$$E^c(\infty) = + \frac{\hbar^2}{2Ma^2} = \frac{m}{M} \text{ rydberg}, \quad (9)$$

where m/M is the ratio of electron and proton mass. This value is nothing else but the correction for the relative motion between the electron and one nucleus to which it is associated in the separated system $H + H^+$.

(2) $R \rightarrow 0$. In this limit of the united atom, $\alpha \rightarrow 2$, $\beta \rightarrow 1$ and

$$E^c(0) = \frac{m}{M} \frac{\hbar^2}{2ma^2} \left[\frac{4+1}{2} - \frac{1}{2} \right] = 2 \left(\frac{m}{M} \right) \text{ rydberg}, \quad (10)$$

which is the correction for the relative motion between the electron and the nucleus of helium ion of mass 2.

The value $E^c(\infty) = (m/M) \text{ rydberg}$ should be incorporated into the asymptotic energy of the separated system $H + H^+$, and the part of the correction for the coupling between the electronic and nuclear motion which is relevant in considering the effective potential for the nuclear motion given by Eq. (2) is

$$\Delta E(R) = E^c(R) - E^c(\infty). \quad (11)$$

The values of $E^c(R)$ given by (8) depend on the values of the parameters $\alpha(R)$ and $\beta(r)$, which have to be determined by the variational method. In the figure, we have given the value $\Delta E(R)$ for the simpler wave function $\alpha(R) = \beta(R)$, after α has been calculated by a variational calculation of the energy of H_2^+ (for fixed nuclei) as a function of R . While the exact values of

$E^c(R)$ depend on the wave function ψ employed, the qualitative feature of a repulsive potential $E^c(R)$ having the asymptotic values (a) and (10) is quite independent of the exact form of the wave functions ψ . From Fig. 1, it is seen that for distances $R \simeq 6a$ where the van der Waals potential is appreciable, the contribution $E^c(R) - E^c(\infty)$ from the correction for the coupling is not negligible.

It may further be remarked that the asymptotic dependence on R of the expression (8) is not correct, since the wave function (4) takes no cognizance of the effect of the other nucleus B on the wave function of the electron in the neighborhood of A . This polarization effect can be included by writing the "atomic orbital" in the perturbation theory

$$\psi_n(\mathbf{r}_A) = \psi_n^0(\mathbf{r}_A) + \sum_k' \frac{\int \psi_n^{*0}(\mathbf{r}) V' \psi_k(\mathbf{r}) d\tau}{E_n^0 - E_k^0} \psi_k^0(\mathbf{r}_A), \quad (12)$$

where

$$V' = -\frac{e^2}{r_B} - \frac{e^2}{R} + \frac{e^2}{R^2} z_A$$

for R large, where z_A is the z -component of the radius vector \mathbf{r}_A . The molecular orbital is then

$$\Psi(\mathbf{r}, X_A, X_B) = N[\psi_n(\mathbf{r}_A) + \psi_n(\mathbf{r}_B)]. \quad (13)$$

For large R , it is permissible to neglect the overlap of the atomic orbitals centered at the nuclei A and B . If we regard the ψ_k^0 to be the normalized hydrogenic wave functions, then

$$2N^2 = 1 + \frac{e^4}{R^4} \sum_k \frac{|Z_{nk}|^2}{(E_n^0 - E_k^0)^2}, \quad (14)$$

where $Z_{nk} = \int \psi_n^0 z \psi_k^0 d\tau$. One may introduce the oscillator strength f_{nk} :

$$f_{nk} = \frac{m}{\hbar^2} (E_n^0 - E_k^0) |Z_{nk}|^2. \quad (15)$$

For convenience, we denote by

$$S = \sum_k \frac{|f_{nk}|}{\left| 1 - \frac{1}{k^2} \right|^3}, \quad c = 1 + \frac{8}{\rho^4} S, \quad (16)$$

where for the continuum, k^2 is to be replaced by $-k^2$. Calculations then gives

$$\begin{aligned} \int \Psi \frac{d^2}{dR^2} \Psi d\tau &= -N^2 \int \left(\frac{d\psi}{dR} \right)^2 d\tau + \left(\frac{1}{N} \frac{dN}{dR} \right)^2 \\ &\simeq -\frac{32}{a^2 c} \left(1 - \frac{8S}{c\rho^4} \right) \frac{1}{\rho^8}, \end{aligned} \quad (17)$$

where $\rho = R/a$. The sum S can be calculated,⁴ and for the $1s$ state of H , one finds

$$S \simeq 1.23,$$

and

$$E^c(R)' = 9.2 \times 10^{-13} \left(1 + \frac{10}{\rho^4}\right)^{-1} \times \left[1 - \frac{1}{2} \left(\frac{2}{\rho}\right)^4 S \left(1 + \frac{10}{\rho^4}\right)^{-1}\right] \frac{1}{\rho^6} \text{ in erg/mole.} \quad (18)$$

This inverse 6th power variation is the result of the polarization effect. It is $\simeq 0.2 \times 10^{-15}$ erg/mole at $R = 4a$, $\simeq 0.06 \times 10^{-15}$ erg/mole at $R = 5a$, and at these distances, $E^c(R)'$ is smaller than the $E^c(R)$ calculated in (8). For large R , the expression $E^c(R)$ in (8), which neglects this polarization effect, decreases exponentially with R . To a first approximation, one may regard the total coupling correction as represented by the sum of $E^c(R)$ and $E^c(R)'$ in (8) and (18).

$^1\Sigma, ^3\Sigma$ State of Hydrogen Molecule H_2

The coupling between the electronic and the nuclear motions in the lowest $^1\Sigma, ^3\Sigma$ states of H_2 can be treated with the wave function of Wang.⁵

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2, X_A, X_B) &= N [\exp(-\alpha(r_{1A} + r_{2B})/a) \\ &\quad \pm \exp(-\alpha(r_{1B} + r_{2A})/a)], \\ N^2 &= \left(\frac{\alpha}{a}\right)^3 \frac{2}{(2\pi)^2} \left[1 \pm e^{-2x} \left(1 + x + \frac{x^2}{3}\right)^2\right]^{-1} \\ &\equiv \left(\frac{\alpha}{a}\right)^2 \frac{2}{(2\pi)^2} Q^{-1}, \quad (19) \\ x &= \frac{\alpha R}{a} \equiv \alpha \rho. \end{aligned}$$

Entirely similar calculations as for H_2^+ lead to the following expression:

$$\begin{aligned} E^c(R) &= 2 \left(\frac{m}{M}\right) \left(\frac{\hbar^2}{2ma^2}\right) \alpha^2 \\ &\times \left[1 \mp \frac{e^{-2x}}{Q} \left(1 + 2x + \frac{14}{9}x^2 + \frac{4}{9}x^3\right) \right. \\ &\quad \left. - \frac{e^{-4x}}{9Q^2} x^2 (1+x)^2 \left(1 + x + \frac{x^2}{3}\right)^2 \right. \\ &\quad \left. + \text{terms in } \frac{d\alpha}{d\rho}, \frac{d^2\alpha}{d\rho^2} \right]. \quad (20) \end{aligned}$$

The value $E^c(\infty) = 2(m/M)$ rydberg at infinite separations is the correction for the relative motion between

the electron and nucleus in the two H atoms. At $R \rightarrow 0$, $\alpha \rightarrow \alpha_0$ and $E^c(R) \rightarrow \alpha_0^2(m/M)$ ry for the $^1\Sigma$ state where α_0 is the effective charge of each electron in the helium-like atom with atomic mass 2. For $^3\Sigma$ state, $E^c(0) \rightarrow \infty$. This is understandable on the view that $E^c(R)$ is in general of the order m/M times the electronic energy of the system, and for the repulsive $^3\Sigma$ state of H_2 , the electronic energy (apart from the e^2/R term) in the approximation (19) becomes infinite as $R \rightarrow 0$. The correction for the coupling, referred to the corrected energy of the separated atoms $H+H$, is given by

$$(\alpha_0^2 - 2) \left(\frac{m}{M}\right) \text{ rydberg} > E^c(R) - E^c(\infty) > 0, \quad (21)$$

which decreases from $(\alpha_0^2 - 2)(m/M)$ rydberg at $R = 0$ to 0 at $R \rightarrow \infty$. The exact values of $E^c(R)$ in (20) have to be calculated with the values of the parameter $\alpha(R)$, which are to be obtained by a separate variational calculation of the electronic energy of the H_2 molecules for various values of the distance R . These calculations of $\alpha(R)$ and $E^c(R)$ are being made and the result will be reported in the future.

For very large distances R , the asymptotic dependence of $E^c(R)$ in (20) is not correct since the wave function (19) again does not include the effect of polarization. Entirely similar calculations to that for H_2^+ in (12)–(18) shows that, on including this polarization effect, one obtains a correction for large R given by

$$E^c(R) = E^c(\infty) + \frac{54}{\rho^8} \left(2 \frac{m}{M} \text{ rydberg}\right) + O\left(\frac{1}{\rho^{10}}\right),$$

where $\rho = R/a$. At $\rho = 3$, this term in ρ^{-8} is about m/M times the van der Waals energy $-12/\rho^6 (\hbar^2/2ma^2)$.

CONCLUDING REMARKS

From this work it is clear that the effect of the coupling between the electronic and the nuclear motion in a molecule is to give rise to a repulsive potential which in the limits of the united atom and the separated atoms is simply the familiar correction for the relative motion between the electrons and the nucleus in each atom. The energy correction relative to the corrected energy of the separate atoms is represented by a repulsive potential represented by $E^c(R) - E^c(\infty)$ in (21). This correction has to be applied to the usual "potential" for the nuclear motion obtained by the static nuclei approximation. The magnitude of this correction at distances of a few units of the Bohr radius a is of the same general order as the van der Waals potential in the case of the lighter atoms such as H and He . For heavy atoms, this correction is small and may be neglected.

The inclusion of the correction $\Delta E = E^c(R) - E^c(\infty)$ in (11) in the equation for the nuclear motion (3) has the interesting consequence that the effective potential $V(R)$ in (2) is dependent on the masses of the atoms and is hence different for different isotopic molecules,

⁴ See, for example, Bethe's article, *Handbuch der Physik* (Springer-Verlag, Berlin, Germany, 1933), Vol. 24/1, p. 443.

⁵ S. C. Wang, Phys. Rev. 31, 579 (1928).

such as H_2 , HD , D_2 , He_2^4 , He_2^3 . It is interesting to note that the information concerning the van der Waal's potential between two helium atoms from the second virial coefficient data seems to indicate the possible existence of a bound state in He_2^4 and the nonexistence of a bound state in He_2^3 .⁶ It is seen from (2) that the

⁶ T. Kihara, J. Phys. Soc. Japan, **10**, 249 (1955); T. Kihara and S. Kaneko, *ibid.* **10**, 314 (1955).

lighter isotopic molecule will have a larger (repulsive) correction $E^c(R)$, which will lead to a shallower trough in the van der Waal's potential. Thus, apart from the mass factor M in (3), the correction $E^c(R)$ also contributes to a smaller binding or stability for the lighter isotopic molecules He_2^3 compared with He_2^4 . A similar treatment of the problem for two helium atoms will be given in a forthcoming paper.

Free Radicals by Mass Spectrometry. VIII. The Ionization Potentials of *Para*-, *Ortho*-, and *Meta*-Xylyl Radicals*

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The vertical ionization potentials of the *para*-, *ortho*- and *meta*-xylyl radicals as measured by electron impact are found to be 7.46 ± 0.03 , 7.61 ± 0.05 , and 7.65 ± 0.03 v, respectively. The thermal dissociation of the *para*- and *ortho*-xylyl radicals to form the quinodimethanes has been observed. The *meta*-xylyl radical was found to have a considerably greater thermal stability.

INTRODUCTION

THE vertical ionization potential of the benzyl radical has been measured by electron impact on radicals produced by the thermal decomposition of benzyl iodide¹ and of benzylamine.² The resulting average value of $I(\text{benzyl}) = 7.76 \pm 0.08$ v is considerably at variance with values of around 8.50 v derived from the appearance potentials of the $C_7H_7^+$ ion from toluene, dibenzyl, and ethyl benzene, and the relevant heats of formation.^{3,4} The latter data lead to a dissociation energy for the $C_6H_5CH_2-H$ bond of 77 ± 3 kcal/mole⁵ in good agreement with the value obtained by Szwarc for this bond by pyrolysis.⁶ Consequently, if the appearance potential of $C_7H_7^+$ from toluene (11.87 ± 0.1 v)³ is combined with the measured $I(\text{benzyl})$ (7.76 ± 0.08 v)² using the equation of the direct method,⁶

$$A(C_7H_7^+) - I(C_7H_7) \geq D(C_7H_7-H),$$

one obtains the result that $D(C_7H_7-H) \sim 95$ kcal, an amount that is greater than 77 ± 3 kcal by the discrepancy between the derived and measured ionization

potentials of benzyl. This dissociation energy seems to be unreasonably high in view of the stability of the benzyl radical, and it would appear that either $A(C_7H_7^+)$ from toluene contains an excess energy term, or that the measured ionization potential of benzyl is too low by ~ 0.8 v. It was thought that measurement of the ionization potentials of xylyl radicals should help to throw some light on the latter possibility. The energy of formation of the benzyl ions reflects the degree of interaction of the substituents with the π electrons of the ring, and the ionization potential of xylyl radicals should be only slightly less than that of benzyl. Furthermore, it might be expected that $I(\text{xylyl})$ should bear the same relation to the ionization potential of the corresponding xylene as $I(\text{benzyl})$ does to $I(\text{toluene})$.

It is also of interest to know the effect of the position of methyl substitution on the energy of the π electrons of the free radical. It is of particular importance to know how the ionization potential of the aromatic radical is affected by methyl substitution for the rates of various reactions have been interpreted on the basis of assumptions about the magnitude of this effect.^{7,8}

EXPERIMENTAL

The *para*-, *ortho*-, and *meta*-xylyl iodides were prepared from samples of the bromides obtained from the Eastman Kodak Company. The bromide was added drop-wise to a saturated solution of sodium iodide in acetone, the iodide precipitated by the addition of water, washed, and purified by several fractional

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¹ Lossing, Ingold, and Henderson, J. Chem. Phys. **22**, 621 (1954).

² Farmer, Henderson, McDowell, and Lossing, J. Chem. Phys. **22**, 1948 (1954).

³ D. O. Schissler and D. P. Stevenson, J. Chem. Phys. **22**, 151 (1954).

⁴ F. H. Field and J. L. Franklin, J. Chem. Phys. **22**, 1895 (1954).

⁵ M. Szwarc, J. Chem. Phys. **16**, 128 (1948).

⁶ D. P. Stevenson, J. Chem. Phys. **10**, 291 (1942).

⁷ A. G. Evans, Trans. Faraday Soc. **42**, 719 (1946).

⁸ A. G. Evans, *Reactions of Organic Halides in Solution* (Manchester University Press, Manchester, 1946).