We index the extrema in Q from high to low velocity, starting with $N=1$ for the first maximum, $N=1.5$ for the minimum which follows, etc., to $N=M$ for the maximum at lowest v. Analysis of the MM derivation reveals that the condition for greatest deviation from Q_{MM} is $\eta_N{}^m=\pi(N-\frac{1}{4})$. A semiclassical treatment[4] shows that the maximum reduced phase depends solely upon $K\equiv\frac{1}{2}\mu v^2/\epsilon$, increasing monotonically with decreasing K. Also, l_m decreases toward zero as $k\equiv\mu v/\hbar$ decreases, so that $\eta^m(k)$ approaches $\eta_0(0)$. In the low-energy region the semiclassical approximation loses validity, and a partial wave analysis[1] is required. We note that, rigorously, $\eta^m(0)<\eta_0(0)+\pi/2$; in addition, considerations based on scattering-length theory

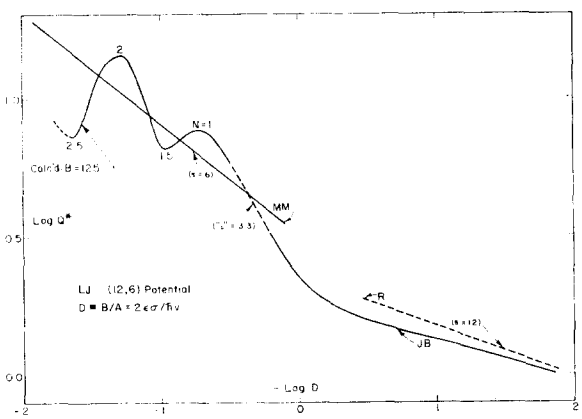

FIG. 1. Velocity dependence of the cross section.

strongly suggest[5] that $\eta^m(k)<\eta^m(0)$. By Levinson's theorem[6] $\eta_0(0)=n\pi$, where n is the number of discrete levels of zero angular momentum. Thus $N<n+\frac{3}{4}$, so that $M=n$; i.e., the number of maxima in $Q(v)$ equals the number of bound vibrational states of the di-atom.

Returning to the semiclassical analysis,[4] we obtain for the LJ (12,6) potential $\eta^m=(120\pi/847)(231/160)^{1/6}D\cdot g(K)$, where $D\equiv B/A=2\epsilon\sigma/\hbar v$ and $g(K)=1-0.25K^{-\frac{1}{2}}+\cdots\cong 1-0.25DB^{-\frac{1}{2}}$ (valid for $D\leq 2B^{\frac{1}{2}}$). With the previous formula for $\eta_N{}^m$ this yields $N-\frac{1}{4}=0.3012(\epsilon\sigma/\hbar)v_N{}^{-1}[1-0.354(\epsilon/\mu)^{\frac{1}{2}}v_N{}^{-1}]$, where v_N is the velocity of the Nth extremum. A plot of $N-\frac{1}{4}$ vs $v_N{}^{-1}$ must pass through the origin; this serves to verify the assignment of the indices to the extrema. The initial slope of the line yields $\epsilon\sigma$; the curvature is governed by ϵ/μ. In addition, one may plot $(N-\frac{1}{4})v_N$ vs $v_N{}^{-1}$; the ratio of slope to intercept yields separately ϵ, but with low sensitivity.

Consider next the "high-velocity" region (criterion: $\eta^m<\frac{1}{2}$). Using the Jeffreys–Born (JB) approximation for the LJ (12,6) phase[1] one obtains, upon rederiving the MM equation

$$Q_{\mathrm{JB}}{}^*=\beta_1{}^2\{2+(1/10)(63\pi/128)^2D^2\beta_1{}^{-22}\times[1-(640/147)\beta_1{}^6+(2560/441)\beta_1{}^{12}]\},\quad(1)$$

valid for $D\leq 1$, and usable as an approximation (within a few percent) to $D\cong 3$. Here β_1 is the root of $\beta^{11}+(3\pi/4)D\beta^6-(63\pi/128)D=0$, where $\beta=(l+\frac{1}{2})/A$. As $D\rightarrow 0$, asymptotically $\beta_1\sim 1.0404D^{1/11}$ and $Q_{\mathrm{R}}{}^*\sim(21/10)(63\pi/128)^{2/11}D^{2/11}=2.273D^{2/11}$, as expected for an inverse power ($s=12$) repulsive potential. This is to be compared with $Q_{\mathrm{MM}}{}^*=3.170D^{2/5}$ ($s=6$ attraction only[1]). Figure 1 shows a graph of Eq. (1), labeled JB; the straight lines R and MM designate $Q_{\mathrm{R}}{}^*$ and $Q_{\mathrm{MM}}{}^*$. Shown also is an example of a curve of Q^* in the "low-velocity" region ($D\geq 3$), calculated[1] via the standard partial wave procedure, for $B=125$. The "wavelength" of the undulatory deviations decreases with increasing $\epsilon\sigma$, making resolution more difficult. Further discussion, including a consideration of the "amplitude" of the undulations (which decreases with increasing μ), is deferred to a detailed paper in preparation.

Applying the present procedures to the data of reference 2, one obtains for Li–Xe and K–Xe values for $10^{22}\epsilon\sigma$(erg cm) of 9.4_5 and 6.7_2, respectively. Indexing of the extrema thus far observed[2] implies a minimum of three vibrational states each for the LiXe and KXe molecules in the $^2\Sigma^+$ state.

† Supported by the U. S. Atomic Energy Commission Div. of Research.

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[2] E. W. Rothe, P. K. Rol, S. M. Trujillo, and R. H. Neynaber, Phys. Rev. (to be published).
[3] For simplicity we limit consideration to unlike atom collisions involving one $^1S_0$ state atom (Group II or VIII) and one either $^1S_0$ or $^2S_{\frac{1}{2}}$ (Group I), yielding the single molecular state $^1\Sigma^+$ or $^2\Sigma^+$.
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[5] It has not been possible to prove this in general, however. Thus in unfavorable circumstances it is possible that $M=n+1$.
[6] See P. Swan, Proc. Roy. Soc. (London) **A228**, 10 (1955); in the present case[3] Pauli excluded states are not involved.

Alternating Linewidths in the ESR Spectra of Dinitrobenzene Anion Radicals*

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WE have found an alternation in the linewidths in the ESR spectrum of the anion radical of *m*-dinitrobenzene. The radical was produced by electrolytic reduction in N,N-dimethyl-formamide solution at room temperature. The derivative spectrum obtained at −50°C shows that those hyperfine components corresponding to $m_{\mathrm{N}}=\pm 1$ (where m_{N} is the total z component of the nitrogen nuclear spin angular momentum) are considerably broader and of smaller amplitude than those for which $m_{\mathrm{N}}=\pm 2.0$. At room temperature, the effect is much weaker but may be detected by careful analysis of the spectrum. Examination of the spectra of the *p*- and *o*-dinitrobenzene

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anions under identical conditions failed to show any indication of alternating linewidths.

Alternating linewidths have previously been reported for the dinitrodurene anion[1] and the dihydroxydurene cation.[2,3] They were attributed in part to the steric crowding of the four methyl groups. The existence of an alternating linewidth in the *m*-dinitrobenzene anion is thus unique and unexpected. Furthermore, its absence in the ortho and para isomers indicates that the meta compound must have some special property.

The models previously outlined[1] to account for the alternating linewidth in the dinitrodurene anion may be extended to the present case. We consider two nitrogen nuclei with time-dependent splitting constants, $a_1^N(t)$ and $a_2^N(t)$, having the same average value. It can be shown that time-dependent fluctuations in sign and/or magnitude of their difference $[a_1^N(t)-a_2^N(t)]$, is sufficient to cause an alternating linewidth.[4] Two

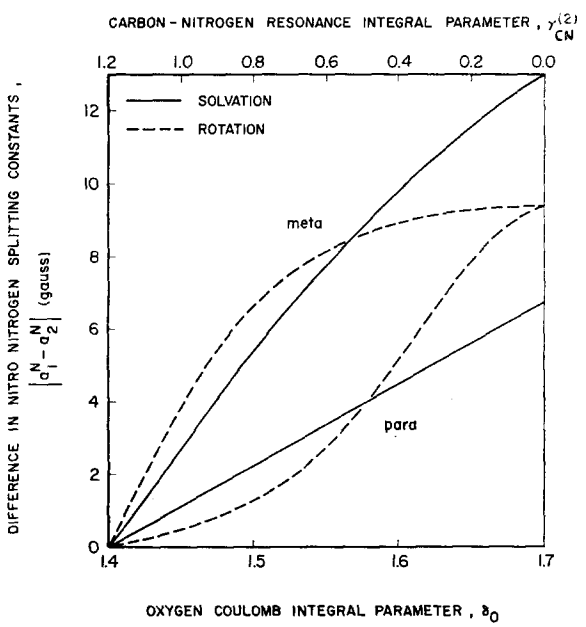

FIG. 1. Plot of the nitrogen splitting constant difference, $|a_1^N-a_2^N|$, for the *meta*- and *para*-dinitrobenzene anions as a function of the Coulomb-integral parameter δ_O (solvation) and the resonance-integral parameter γ_{CN} (rotation) of one nitro group. Parameters for the other nitro group are held constant with $\delta_O=1.4$ and $\gamma_{CN}=1.2$.

mechanisms are suggested to modulate the a_i^N: (1) collisions with solvent molecules which force the nitro groups out of the plane; or, (2) the formation of short-lived solvent complexes. Either mechanism causes a redistribution of spin density in the radical, and we further assume (see below) that both result in the required time-dependent fluctuations.

Molecular-orbital calculations of the Hückel–LCAO type with the addition of the approximate configuration interaction treatment of McLachlan[5] were performed to test the assumptions about splitting constant changes, and to determine whether or not a difference would be expected between the meta and para isomers. The solvation of the oxygen atoms of one nitro group was represented by allowing the Coulomb integral of the oxygen atom α_O to increase in magnitude,[6] and a rotation of one nitro group was represented by decreasing the resonance integral β_{CN} between the nitrogen atom and the ring. The parameters used for an unsolvated, in-plane nitro group were[7] $\delta_N=2.2$, $\delta_O=1.4$, $\gamma_{CN}=1.2$, and $\gamma_{NO}=1.69$, where $\delta_X=(\alpha_X-\alpha)/\beta$, and $\gamma_{XY}=\beta_{XY}/\beta$ in the usual notation. The splitting constants were calculated from the semiempirical formula[7] $a^N=99.0\rho_N^\pi-71.6\rho_O^\pi$, where ρ_N^π and ρ_O^π are the pi-electron spin densities on the nitrogen and oxygen atoms, respectively. The calculations show that if nitro group 1 is solvated, a_1^N becomes greater than a_2^N, while if it is rotated out of the plane, a_1^N becomes less than a_2^N. Thus these mechanisms induce the fluctuations in $[a_1^N(t)-a_2^N(t)]$ required to produce an alternating linewidth. The figure gives the difference $|a_1^N(t)-a_2^N(t)|$ as a function of solvation and rotation, and clearly shows that the meta isomer is more influenced by both effects than the para isomer. In the limit of large interactions, these mechanisms are equivalent to a jumping of the unpaired electron between nitro groups that results in a time-dependent change in sign of the large difference $[a_1^N-a_2^N]$. The MO calculations also show that the bond order of the C–N bond is somewhat smaller in the meta than in the para isomer. This result suggests that the meta compound is the isomer more easily subjected to rotational motions out of the planar conformation. Valence-bond theory predicts a similar difference in bond order because a quinoid structure can be written for the para isomer but not for the meta compound. Since the MO calculations show that the solvation of one nitro group increases its bond order at the expense of the bond order of the other nitro group, and that this effect is larger in the meta than in the para isomer, a coupling of the rotation and solvation mechanisms is also possible. The ortho and para radicals would be expected to be similar except that, because of steric interference, the two nitro groups in the ortho compound are normally not quite planar with the ring, and their close proximity may make it impossible to solvate one group preferentially.

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