On the Existence of SteadyState Detonations Supported by a Single Chemical Reaction

W. W. Wood and J. G. Kirkwood

Letters to the Editor

Announcement

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Communications
Comments and Errata
Notes

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Letters in this category are brief preliminary announcements, limited to 600 words, of important current results. It is assumed that in most cases the details of such work, in a completed form, will be published at a later date. These letters are not sent for review, although the Editor will in many cases submit them to readily available experts in order to ascertain their suitability for this section. All such Letters received not later than the 15th of the month will appear in the issue of the second month following. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents.

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Letters in this category include the usual errata and also comments by authors or others on previously published work and are limited to 600 words. Comments by others than the authors of the already published work being discussed in such Letters will normally be submitted to the authors for review. The author's adverse criticism will not be taken as adequate reason for rejection. It will also be usually the case that the author will be given the opportunity of submitting a rebuttal to be printed immediately following these comments. In all such cases the publication of both the comments and the rebuttal will be delayed until such time as each party has had an opportunity to examine the final statement of the other on the matters under discussion. The two Letters will then be published simultaneously. In all these cases where it seems desirable the Editor will recommend that a single joint comment by the two parties concerned be published in this section. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents.

Notes

Letters in this category have the character of short articles. They are limited to 600 words. These Letters will be reviewed in the same manner as that in which articles are reviewed. They will be published according to the normal schedule for articles, i.e., if received and accepted not later than the 15th of the month will appear in the issue of the third month following, and not in chronological order with date of receipt of regular articles. The reviewers will be asked by the Editor to judge these Letters according to the same standards as those employed in the case of regular articles, except insofar as it must be taken into consideration that their brevity necessarily imposes various restrictions on their authors. It will normally be assumed that the same work reported in these Notes will not be published in extended form at a later date although, of course, further work may result in a longer article.

No proof will be sent to the authors of "Communications" and "Comments and Errata". Proof will be sent to authors of "Notes". The publication charge for Letters is $25 per page, with a minimum of $25 per Letter. If honored, the Institution will be entitled to 100 reprints without covers.

On the Existence of Steady-State Detonations Supported by a Single Chemical Reaction*

W. W. Wood, *Los Alamos Scientific Laboratory, Los Alamos, New Mexico*
AND
J. G. Kirkwood, *Yale University, New Haven, Connecticut*
(Received October 1, 1956)

FOR one-dimensional flow in a reacting fluid, we showed[1] that the characteristic sound velocity is the "frozen" or high-frequency value c_0, as distinguished from the "equilibrium" or low-frequency value c. For detonations we assumed the existence of von Neumann[2]-type solutions, in which a steady-state reaction zone is followed by a time-dependent rarefaction, and showed that such solutions require a Chapman-Jouguet (CJ) condition involving c_0. This agreed with the conclusions of Zeldovitch,[3] and Brinkley and Richardson.[4] Here we show that such solutions fail to exist for a process involving a single reversible reaction.

In our previous notation,[1] we consider only the case $\sigma > 0$. Then the frozen CJ point C_0 (Fig. 1), satisfying $D - u = c_0$, lies on the
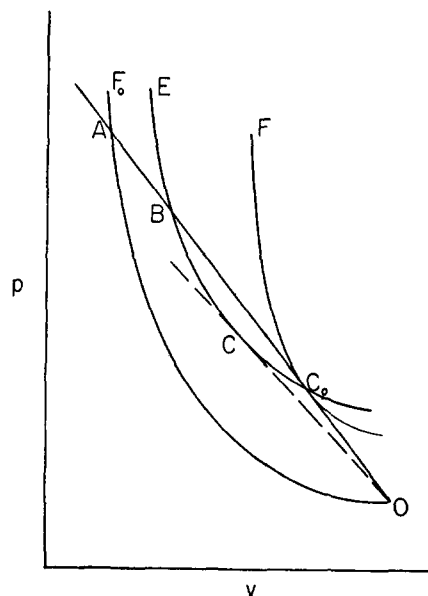

FIG. 1. p-v diagram for the detonation process.

equilibrium Hugoniot E. At any point of E, a fixed composition Hugoniot can be constructed. At C_0, the straight line OC_0 from the initial point O is tangent to such a fixed composition Hugoniot F. It is important to establish the position of C_0 with respect to point C, where OC is tangent to E. C satisfies the relation $D - u = c$; we will call it the "equilibrium CJ point." If the equilibrium equation of state has the usual properties, Jouguet's rule[5] states that for points of E above C (strong detonations), $(D-u)^2 < c^2$. It follows[6] that C_0 cannot lie above C, since then $c_0^2 = (D-u)^2 < c^2$, while thermodynamic stability requires $c_0^2 > c^2$. Therefore C_0 lies below C.

Consider the proposed steady-state detonation in which the reaction zone terminates at C_0. The conservation laws require all state points to lie on the straight line through O and C_0. The initiating shock brings the material to point A, the intersection of this line with the Hugoniot F_0 for the unreacted explosive. Reaction begins and the state point moves down along OC_0A, which intersects E at some point B above C. Because of the condition $\sigma > 0$, only one value of λ is possible for given p, v so that when the state point reaches B it is necessarily in an equilibrium state. In its neighborhood the over-all reaction rate must be approximately first order. It is then easy to show that B is reached

only asymptotically (infinite Lagrangian time) from above. C_0 is never reached; even if the state point were to pass B, it would be forced back since properties of the equation of state similar to those leading to Jouguet's rule will result in r changing sign when E is crossed.

Since at large distances behind the wave front, the mass velocity approaches u_B, directed toward the unreacted explosive, we conclude that the solution proposed is not a "free" wave, but is instead an everywhere-steady driven wave supported by a piston moving with velocity u_B. Since the wave corresponding to OC_0A was the only possible solution of the von Neumann type, we conclude that such solutions do not exist for the present case. Steady-state conditions in the reaction zone, strictly speaking, can only be approached asymptotically. The theory in its present form does not describe this asymptotic state. The steady-state theory, to date the only feasible analytical approach, leads only to a one parametric family of everywhere-steady piston supported flows, the one of minimum propagation velocity and piston velocity having as final state the "equilibrium CJ point" C. It should be mentioned that von Neumann[2] considered only the case of an irreversible reaction going to completion, in which case the distinction between c_0 and c, C_0, and C disappears.

Our discussion does not apply to the case of more than one reaction process, which is presently under consideration.

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[2] J. von Neumann, OSRD–549 (1942).
[3] Y. B. Zeldovitch, J. Exptl. Theoret. Phys. (USSR) **10**, 542 (1940).
[4] S. R. Brinkley, Jr., and J. M. Richardson, *Fourth Symposium (International) on Combustion* (Williams and Wilkins, Baltimore, 1953), p. 450.
[5] R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Interscience Publishers, Inc., New York), p. 204.
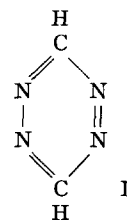[6] W. Fickett (private communication).

Electronic Structure of s Tetrazine

LEONELLO PAOLONI
Laboratorio di Chimica Terapeutica, Istituto Superiore di Sanità, Roma
(Received October 15, 1956)

THE semiempirical theory of electronic spectra proposed by Pariser and Parr[1] has met with considerable success not only when applied to unsaturated hydrocarbons but also in the case of conjugated N-heterocyclic molecules. But as far we know no treatment has yet been reported of molecules having two adjacent nitrogen atoms. When recently internuclear distances and bond angles of s tetrazine became available[2] we thought it interesting to see whether the Pariser and Parr method could account for its observed spectrum.[3] This implies the choice of a suitable value for the resonance integral β_{NN}, which might then be used in the study of other molecules, also for ascertaining to what extent the semiempirical procedure allows reliable results.

s Tetrazine (I) is a planar molecule, whose hexagonal benzene-like ring makes the benzene MO's the most convenient starting eigenfunctions. Our treatment follows therefore that outlined by Pariser and Parr.[1] Changes have been made (i) in the choice of $(pp|pp)$ integrals, which were obtained through the empirical relationship $(pp|pp) = 3.29_4 Z_p$ ev, discussed in a recent paper[4]; (ii) in the evaluation of the $(pp|qq)$ integrals, for which theoretical values were used[5] on distances $\geqslant 2.8$ A; (iii) in the penetration integrals, which were all neglected. Results are collected in Table I. They are obtained with the β_{CN} value -2.74 ev deduced[6] from the observed spectrum of s triazine and previously used for melamine,[7] and with a $\beta_{NN} = -2.35$ ev, chosen to fit the observed spectrum of s tetrazine. Here[3] the weak band at about 520 mμ is considered as $\pi - n$, while the strong band with peak at 252.5 mμ (4.91 ev) is regarded as due to the first singlet-singlet, $\pi - \pi$, transition. The second calculated transition, $^1B_{2u} \leftarrow {}^1A_{1g}$, is expected near 210 m$\mu$ and less intense than the first one, whereas the singlet-triplet transitions at 325 to 350 mμ fall in a region which is

TABLE I. Calculated excited energy levels of s tetrazine.

State	Energy (ev)	Oscillator strength
$^1B_{3u}$	4.91	0.103
$^1B_{2u}$	5.85	0.019
$^3B_{3u}$	3.60	0
$^3B_{2u}$	3.89	0

given as nearly transparent in the published spectrum[3]: lack of experimental data prevents therefore a further check of the present results.

Work is now well advanced in which 3,6-diamino-1,2,4,5-tetrazine, described by Lin et al.,[8] is treated according to the procedure previously followed for melamine.[7] The β_{NN} integral here found will be used, so that no new empirical parameters need to be introduced in the calculations. The results will be published in full elsewhere.

$$
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H \\
C \\
N \diagup\!\!\diagup \quad \diagdown N \\
\mid \qquad \qquad \| \\
N \qquad \qquad N \\
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C \qquad I \\
H
\end{array}
$$

[1] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953).
[2] Bertinotti, Giacomello, and Liquori, Acta Cryst. **9**, 510 (1956).
[3] A. M. Liquori and A. Vaciago, Ricerca sci. **26**, 181 (1956).
[4] L. Paoloni, Nuovo cimento X, **4**, 410 (1956).
[5] R. Pariser, J. Chem. Phys. **24**, 250 (1956).
[6] Hirt, Halverson, and Schmitt, J. Chem. Phys. **22**, 1148 (1954).
[7] M. J. S. Dewar and L. Paoloni, Trans. Faraday Soc. (to be published).
[8] Lin, Lieber, and Horwitz, J. Am. Chem. Soc. **76**, 427 (1954).

Raman Spectrum of Thionyl Bromide*

H. STAMMREICH, ROBERTO FORNERIS, AND YARA TAVARES
Department of Physics, Faculty of Philosophy, Science and Letters, University of São Paulo, São Paulo, Brazil
(Received October 2, 1956)

THIS note reports the complete Raman spectrum of $SOBr_2$ with an assignment of the observed frequencies. No spectral data regarding this molecule were found in the literature; however the spectra of the similar oxyhalides SOF_2, $SOCl_2$, and $SeOCl_2$ have been investigated. Electron diffraction data on $SOCl_2$ and $SOBr_2$ support strongly a pyramidal structure of these molecules[1] possessing but one element of symmetry, namely, a plane containing the sulfur and the oxygen nucleus normal to the SCl_2 or SBr_2 plane. The resulting symmetry belongs to the C_s point group, and therefore we have to expect a Raman spectrum showing four polarized shifts (vibrations of type A'), and two depolarized shifts (of type A''). The planar structure of symmetry C_{2v} formerly assumed by a number of authors should have three vibrations of class A_1 (polarized), two of class B_1, and one of class B_2 (the last three depolarized). More recent Raman[2] and infrared[3] data on the $SOCl_2$ molecule agree better with the assumption of the C_s symmetry.

Thionyl bromide was prepared as described by Mayes and Partington,[4] passing a slow stream of HBr through freshly distilled $SOCl_2$ for twelve hours. The crude product was directly distilled into the Raman tube at 1 mm pressure. $SOBr_2$ decomposes slowly giving off bromine, sulfur monobromide, and sulfur dioxide, changing its original yellow color into deep red.

Due to the darkening of the sample we excited the Raman spectra by the helium radiations 6678 A and 7065 A employing our usual technique.[5] The spectra were recorded on hypersensitized Kodak IN spectroscopic plates; we needed exposure times from one to five hours, and up to ten hours for qualitative polarization