"effective diameter" permit. The fluctuations observed (*1–4*) for the quasi-stellar objects 3C48, 3C196, and 3C273 are of the order of 0.3 magnitudes, or a factor of 1.32 in brightness. A period of 2 years would mean, according to Eq. 6, a source diameter less than 9.2 light-years (8.6 light-years, from Eq. 5). If the night-to-night variations and bright flashes observed for 3C273 and 3C48, amounting to as much as 0.7 magnitude with a period of days (*1–4*), are real and general phenomena, the objects cannot be more than a few light-days in size, as Smith and Hoffleit (*1*) have stated. In the case of a multiple-source disc produced by gravitational contraction, as suggested by Hoyle and Fowler (*5, 8*), the effective diameter would have to be considered to be essentially that of the one source emitting most of the light at a given time, rather than that of the entire assemblage.

It should be kept in mind that Eq. 6 yields an upper limit for the source diameter, not an average, and that the light source would perhaps be considerably smaller than this size. Thus the quasi-stellar objects—at least the optically visible parts—are probably less than a few light-days in size and could be of the order of the solar system in size, or less (*9*). These objects are then many orders of magnitude less than galactic size, simply on the basis of the light fluctuations.

Since the quasi-stellar objects are not of galactic size, it is not absolutely necessary to suppose that they are at the distances of the order of 1000 Mparsec which follow from the application of Hubble's law. The large red shifts observed for these objects (*10–13*) may be due to the same cause as that of the most distant galaxies, or they may be gravitational in origin, or they may simply be due to relativistic velocities of nearby objects. The first explanation requires optical power outputs perhaps 100 times larger than those of the largest and brightest galaxies (*1–3, 5*) and is so far the favorite explanation, although the energy source is not clear. The gravitational explanation is usually ruled out (*5, 10, 12*) primarily on spectroscopic grounds.

The third possibility, that the objects might be much closer to our galaxy, with the red shift due only to the relativistic Doppler shift, has not been much discussed. A minimum distance is determined by the lack of observed proper motion. W. H. Jefferys (*14*) has established the proper motion of 3C273 as unobservably small (0.001 ± 0.0025 second of arc per year), and W. J. Luyten (*15*) has obtained a similar result. If it is assumed, for example, that 3C273 originated near the center of our galaxy, about 8 kparsec (26,000 light-years) from the sun, a proper motion of 0.002 second per year and a recessional velocity of 0.146 *c* (*10*) would correspond to 190 kparsec observed distance, and to an origin about 5 million years ago. This distance is a few galactic diameters away, further than the clouds of Magellan, but not so far as the Andromeda nebula which is about 500 kparsec distant.

How such highly relativistic objects could be produced by an explosion or explosions in our galaxy is not known, and this is probably the principal objection to the idea. Considerable kinetic energy alone would be required, amounting to 1.1 percent of the rest mass for 3C273, and to 9.6 percent for 3C147, the fastest such object yet observed, with $v/c = 0.410$, and $\Delta\lambda/\lambda = 0.545$ (*13*). The optical energy requirements are reduced by a factor of 10^7 at this distance, however, amounting to about 10^5 times the output of our sun. A possible source of high velocities, if the objects are assumed to be local, would be a gravitational collapse (*5, 8*) in our galaxy.

Whatever their distance, it is clear that the quasi-stellar objects are not of galactic size, but are, at least optically, probably less than light-days in size (*16*).

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7. It is interesting to note that a somewhat different case, that of a luminous disc viewed perpendicularly, with waves of brightness spreading out from the center, has precisely the same solution, Eq. 5. In either case an assumed recession of the source would not change the result, but the period *T* should be as measured in the rest frame of the source.
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9. The solar system is about ½ light-day across. These considerations would not rule out an extremely small, dense, region in the center of a galaxy or cluster as a quasi-stellar object, as suggested by S. M. Ulam and W. E. Walden [*Nature* **201**, 1202 (1964)].
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16. A letter by A. T. Young has just been published [*Science* **145**, 72 (1964)], giving some similar considerations on the size of quasi-stellar objects. Young's results are based on square-wave modulation of a light source. If a large spherical source of radius *R* is "turned off" for a time interval *t*, it will undergo a maximum reduction in apparent brightness amounting to $(2ct/R) - (ct/R)^2$. This is, as in Young's example, 19 percent decrease for a 10-light-year-radius source turned off for 1 year. If such a fluctuation were seen, the correct maximum radius would be obtained from Eq. 4 if the period were taken to be $T = \pi t$. This is the period corresponding to the amplitude of the visible fluctuation and its maximum rate of change, for a sinusoidal oscillation. Thus the results of this paper are as applicable to monotonic and single-pulse fluctuations as to sinusoidal oscillations, if the "period" is suitably estimated. Young's formulation and the one given here both give a maximum rate of change of luminosity equal to $2c/R$ logarithmically, or to 1.0857 $(2c/R)$ in units of stellar magnitude.
17. Supported by the AEC. Some of the matters considered have been clarified in interesting discussions with G. R. Burbidge, A. N. Cox, and S. M. Ulam, but they should not be held responsible for the opinions expressed here.

22 June 1964

Pulse Radiolysis of Potassium Bromide Solutions

Abstract. *After application of a 2-microsecond pulse of an electron beam to aqueous, aerated, acid solutions of KBr, transient spectra of Br_2^- and Br_3^- were observed. The kinetic analysis of the reactions as well as the measured values of $G(H_2O_2)$, $G(Br_2)$, and $G(Br_3^-)$ revealed a reaction mechanism differing from the one which is accepted for radiolysis at low intensity.*

In recent pulse radiolysis experiments we have studied the transient species and the yields of hydrogen peroxide in aqueous, aerated $10^{-2}M$ KBr in sulfuric acid at *p*H 2. Pulses of 2-μsec duration of 4 Mev electrons giving up to 5000 rad/pulse were used. The technique has been described elsewhere (*1*). Hydrogen peroxide was determined by the iodide reagent (*2*) after removal of bromine from the solution by bubbling with inert gas.

As shown in Fig. **1**, a transient species appears immediately after the pulse, showing a strong absorption with a maximum at 3600 Å. This transient disappears in about 100 μsec and a new, strongly absorbing transient appears, with a maximum absorption at 2700 Å.

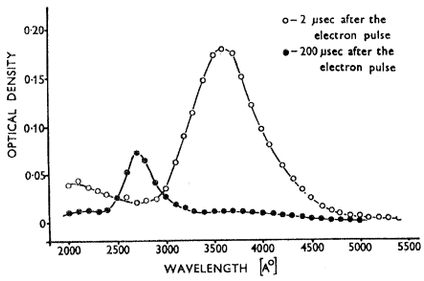

Fig. 1. Transient spectra of aerated $10^{-2}M$ potassium bromide at *p*H 2.1 subjected to pulse radiolysis (pulse of 2-μsec duration). The absorption maximum at 3600 Å is due to the dibromide ion-radical, Br_2^-; the long-lived absorption at 2700 Å is due to the tribromide ion, Br_3^-.

This new transient was stable over a period of at least 2 minutes. By comparison with the data of Grossweiner and Matheson (*3*), and Dorfman *et al.* (*4*), we assign the absorption at 3600 Å to the dibromide ion-radical, Br_2^-. The spectrum of the long-lived species resembled that of a solution prepared by the addition of bromine to $10^{-2}M$ potassium bromide at *p*H 2, and we attribute it to the tribromide ion Br_3^-. We found in a separate experiment that Br_3^- reacts surprisingly slowly with hydrogen peroxide; the optical density due to Br_3^- in a solution of $10^{-2}M$ KBr, $1.5 \times 10^{-5}M$ H_2O_2, and $4 \times 10^{-6}M$ Br_2 at *p*H 2 being decreased only by 47 percent in 4.5 hours. Despite its expected long half-life and its high molar extinction coefficient of 36.000 ± 3.6000 $mole^{-1}$ cm^{-1} we were unable to see absorption due to Br_3^- in γ-radiolysis at a dose rate of 9.2 rad sec^{-1}. Therefore, we attribute the formation of Br_3^- under pulse radiolysis conditions to the high dose-rates used, leading to concentrations of HO_2 radicals such that HO_2 reacts with Br_2^- to yield ultimately H_2O_2 and Br_3^-. We found $G(H_2O_2)$ to be 2.8 ± 0.15. Estimations of the sum of $G(Br_2)$ plus $G(Br_3^-)$ gave 1.5. The rate constant for the reaction of HO_2 with Br_2^- was found to be $(6.4 \pm 0.3) \times 10^9$ $mole^{-1}$ sec^{-1}.

In de-aerated acid potassium bromide ($10^{-2}M$) solutions the Br_3^- absorption was not seen (*3*).

In view of our results, the mechanism for the pulse radiolysis of potassium bromide solutions must be more complex than the mechanism proposed by Allen and Holroyd (*5*) and Sworski (*6*) for radiolysis at low intensities (*7*).

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7. Full details of the pulse radiolysis studies of aerated and de-aerated potassium bromide solutions will be published elsewhere.
8. We thank H. C. Sutton for invaluable comments.
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Molecular Structure of the Synthetic Molecular Oxygen Carrier $O_2IrCl(CO)(P[C_6H_5]_3)_2$

Abstract. *The synthetic molecular oxygen carrier $O_2IrCl(CO)(P[C_6H_5]_3)_2$, discovered by Vaska, has been characterized in a complete molecular structure determination. The structure surmised by Vaska from spectroscopic data has been confirmed and, in addition, definitive details on the attachment of molecular oxygen to iridium in this 1 : 1 reversible oxygen carrier have been obtained. The two oxygen atoms are equidistant from the metal atom, as in Griffith's model of the oxygen atoms in oxyhemoglobin. The O-O bond length of 1.30 ± 0.03 Å is intermediate between those characteristic of O_2 (1.20 Å) and O_2^{-2} (1.48 Å), and corresponds closely to O_2^- (1.28 Å).*

Metal chelate oxygen carriers are of interest both because of the kinetics of oxygen exchange and because of the possible analogy of such carriers to biological oxygen carriers, such as hemoglobin. It is clear from the recent review of Vogt, Faigenbaum, and Wiberley (*1*) that there is little information on how the oxygen molecule is attached to the metal atom in synthetic oxygen carriers. There is some information on the 1:2 complexes, in which one molecule of oxygen is shared between two metal atoms (*2*), but such compounds are not analogous to the oxyhemoglobin system, in which there is one molecule of oxygen for each iron atom. The best characterized of the previously reported 1:1 complexes are the type II *bis*-salicylaldehyde-imine cobalt oxygen carriers (*3*), but in these compounds nothing definitive is known about the bonding which is discussed in terms of the oxygen filling "holes" in the crystal lattice. Moreover these compounds apparently exist in several crystalline modifications, not all of which are active carriers. Recently Vaska (*4*) discovered the 1:1 reversible oxygen carrier $O_2IrCl(CO)(P[C_6H_5]_3)_2$, and this discovery is of great importance since the compound can not only be isolated, but is stable. In this report we summarize our study, by diffraction techniques, of this compound, and we present the first definitive evidence on the mode of attachment of molecular oxygen to the metal atom in a 1:1 synthetic metal-chelate oxygen carrier.

L. Vaska very kindly supplied excellent single crystals of $O_2IrCl(CO)(P[C_6H_5]_3)_2$. These crystals were stable in air during x-ray photography, although they did gradually darken from light orange to orange-brown, without detectable change in the x-ray intensities. The material crystallizes with two molecules in a primitive triclinic cell of dimensions

$$a = 19.02 \pm 0.03, \quad \alpha = 94.0 \pm 0.1,$$
$$b = 9.83 \pm 0.02, \quad \beta = 64.9 \pm 0.1,$$
$$c = 9.93 \pm 0.02 \text{ Å}, \quad \gamma = 93.2 \pm 0.1°,$$

a, *b*, and *c* being the axial lengths and α, β, and γ being the interaxial angles. The unit cell volume is 1678 $Å^3$ and the calculated density 1.61 g/cm^3. A sensitive test for a piezoelectric effect was negative (*5*) and a reasonable structure has been determined on the assumption that the structure is centrosymmetric, space group $P\bar{1}$. The crystal chosen for the x-ray photography had approximate linear dimensions of 0.31 by 0.09 by 0.08 mm and a calculated weight of 3.2 μg. Data were collected at room temperature with MoKα radiation by the equi-inclination Weissenberg technique on a Nonius integrating camera. The intensities were estimated visually against a calibrated strip and were reduced to structure amplitudes F_o in the usual way after a reliable correction for absorption.

The positions of the Ir and P atoms were evident from inspection of the three-dimensional Patterson function.