Table 4. The contribution of various gases, relative to CO_2, to the greenhouse effect. Calculations are based on emitted amounts, and consideration has been given to the gases' decay in the atmosphere. The entry for O_3 refers to amounts formed rather than to amounts emitted.

Species	Relative contribution	
	Mass basis (kg^{-1})	Mole basis (mol^{-1})
CO_2	1	1
CH_4 (direct effects	15	5
CH_4 (including indirect effects)	30	10
N_2O	300	300
O_3*	3	4
CFC-11	4,000	11,000
CFC-12	8,000	20,000

*In the troposphere.

Assume that we produce 1 MJ of energy from natural gas and that a fraction x of the natural gas leaks out before combustion. The emission of greenhouse gases to the atmosphere would then be 56 g of CO_2 (or 1.27 mol) from the combustion and $1.27\,[x/(1-x)]$ mol of CH_4 from the leakage. Each mole of emitted CH_4 is assumed to result in a greenhouse effect corresponding to ten times that of 1 mol of CO_2 (see Table 4). The total greenhouse effect, converted to the equivalent CO_2 emissions, would thus be

$$1.27\left(1+\frac{10x}{1-x}\right)\text{mol of } CO_2 \text{ or}$$

$$56\left(1+\frac{10x}{1-x}\right)\text{g of } CO_2$$

The advantage of converting from oil to natural gas would thus be completely nullified if

$$56\left(1+\frac{10x}{1-x}\right)=78,\ \text{that is, } x\approx 4\%$$

If the spillage of natural gas can be held to 4% or less, there is a net gain in switching from oil to natural gas. This value will actually be higher because CH_4 is also released during the extraction and refining of oil. In consideration of the uncertainties in the calculations of this study, a "break-even" value for natural gas spillage of 3 to 6% is reasonable when comparing oil and natural gas combustion. If the time of integration in Eq. 1 (T) was chosen to be much less than 100 years, the "break-even" value could be even smaller than 3%.

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Defensive Spray of the Bombardier Beetle: A Biological Pulse Jet

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The defensive spray of the bombardier beetle *Stenaptinus insignis* is ejected in quick pulses (at about 500 pulses per second) rather than as a continuous stream. The pulsation may be a consequence of intermittency in the explosive chemical process that generates the spray. The ejection system of the beetle shows basic similarity to the pulse jet propulsion mechanism of the German V-1 "buzz" bomb of World War II.

BOMBARDIER BEETLES, WHEN DISTURBED, emit a jet of defensive spray (Fig. 1A). The fluid stems from two large glands that open at the tip of the abdomen. The abdominal tip acts as a revolvable turret that enables the beetles to aim the spray in all directions (*1*). The ejections appear as a fine mist and are accompanied by audible "pops." The spray effectively deters vertebrate and invertebrate predators (*1, 2*). Its active principles are *p*-benzoquinones (*3*).

The quinones are not stored as such in the glands but are produced explosively at the moment of ejection by the interaction of hydroquinones and hydrogen peroxide with oxidative enzymes (catalase, peroxidases) (*4*). The glands are essentially binary weapons. Each consists of two confluent chambers in which the chemical reactants are separately stored (Fig. 2). Hydroquinones and hydrogen peroxide are stored in the larger, inner chamber of each gland (the reservoir) and the oxidases in the smaller, outer chamber (the reaction chamber). The reservoir is thin-walled, enveloped by muscles, and compressible; the reaction chamber is thick-walled and rigid. A tight valve ordinarily keeps the juncture between the two compartments sealed. Ejections are presumably effected by brief compression of the reservoir. This compression forces reservoir fluid through the inlet valve into the reaction chamber, where the catalytic events leading to quinone formation are initiated.

Thermodynamic calculations had predicted that spray formation should be accompanied by substantial liberation of heat. This was verified empirically: the spray of bombardier beetles is ejected at 100°C (*5*), confirming the observation of early naturalists that seizing large bombardier beetles by hand can be painful (*6*). We report here that the bombardier beetle spray is emitted not as a continuous stream but as a pulsed jet, in analogy with fluid delivery systems known from technology but not from animal glands. Our data were obtained with one species of bombardier beetle, the relatively large (body length ≃ 2 cm) *Stenaptinus insignis* from Kenya.

The first clue to the pulsed nature of the spray stemmed from acoustical recordings (*7*) of the detonations that mark the discharges. Spectrographs (*8*) from these recordings showed that the sound contains a broad range of frequencies (essentially "white noise," as is typical for turbulent, explosive processes) (*9*) and that it is dis-

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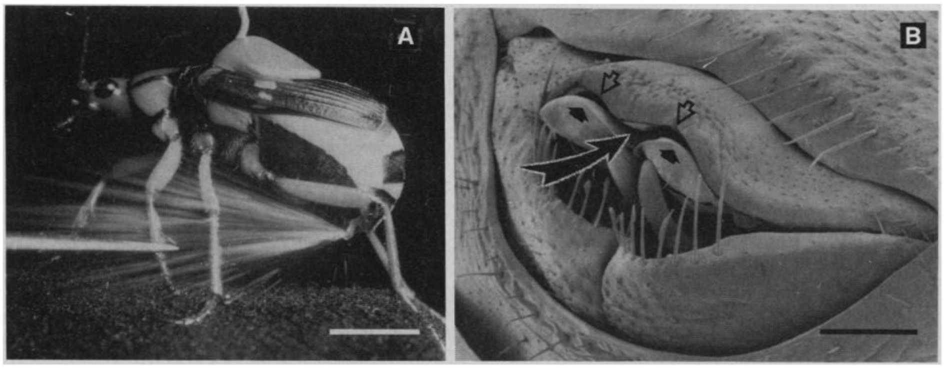

Fig. 1. (**A**) *Stenaptinus insignis* (tethered to a wire fastened to its back with wax) responding to pinching of the left foreleg with forceps by discharging an accurately aimed spray. (**B**) Abdominal tip of a male *S. insignis* showing the curved slit through which spray emerges (open arrows), the site of insertion (large arrow) of the plastic wedge used to pry that slit apart, and the two flanges (small black arrows) that were surgically cut away. Bars: (A) 5 mm; (B) 0.5 mm.

tinctly pulsed (Fig. 3A). Measurements from spectrographs of 45 discharges from seven beetles gave the following values ($\bar{x}$ ± SD): discharge duration = 11.9 ± 4.8 ms (range, 2.6 to 24.1 ms); pulse repetition rate = 531 ± 86 pulses per second (range, 368 to 735 pulses per second); pulses per discharge = 6.7 ± 2.2 (range, 2 to 12).

The possibility that the pulsation was a consequence of the physical vibration of structures associated with the gland openings was early ruled out on the basis of recordings of ejections from one beetle in which a small plastic wedge was inserted so as to pry apart the gland openings, and from another in which the two flanges bordering the lower margin of the gland openings were cut away with a microsurgical scalpel (Fig. 1B). Neither procedure affected the sound modulation of the ejections.

We obtained evidence that the pulsation was indicative of intermittent emission of the spray by causing beetles to discharge on a small force transducer (piezoelectric crystal) (*10*) that registered the impact of the ejected secretion. Simultaneous recordings of the electric output from this crystal, and of the sound of the ejections (*11*), showed a one-to-one match of the electric and sound pulses (Fig. 3B), strongly indicating that the sound pulsation was a concomitant of spray pulsation. We were able to show that the piezoelectric crystal was actually responding to spray impact rather than to airborne sound by causing the beetle to discharge just to the side rather than directly onto the crystal. When this occurred, there was no output from the crystal, and pulsation was picked up by the microphone recording only.

Definitive evidence for the pulsed delivery of the spray was obtained by high-speed cinematography. Fourteen discharges from seven beetles were filmed (2670 and 4000 frames per second) (*12*). The burst-like emission of spray that characterizes the pulsations was clearly resolved in these films (Fig. 4). Frame-by-frame film analysis (measurements of 62 pulses from 11 discharges of four beetles; 4000 frames per second) (*13*) showed spray emergence velocity to be 1163 ± 330 (SD) cm/s (range, 325 to 1950 cm/s). This value is substantially higher than the spray velocity (240 cm/s) recorded for a

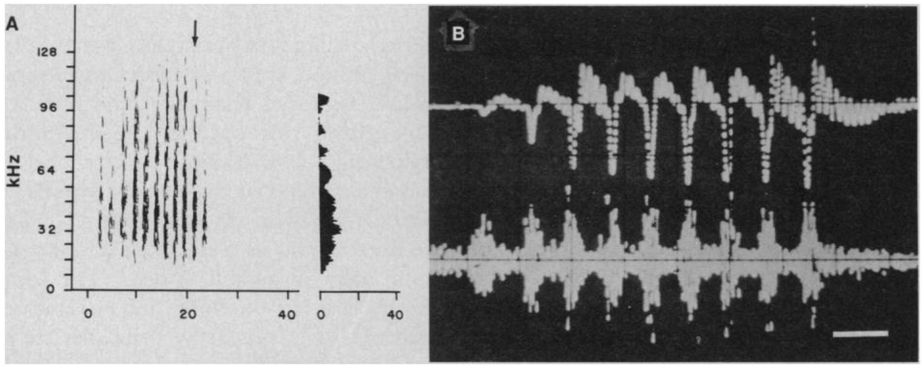

Fig. 3. Physical concomitants of bombardier beetle discharges. (**A**) Sound spectrograph of the discharge; the energy distribution profile on the right was determined at the time denoted by the arrow. (**B**) Simultaneous recordings of the discharge sound (lower trace) and the electric output of a piezoelectric crystal (upper trace) onto which the beetle directed the discharge. Bar, 2 ms.

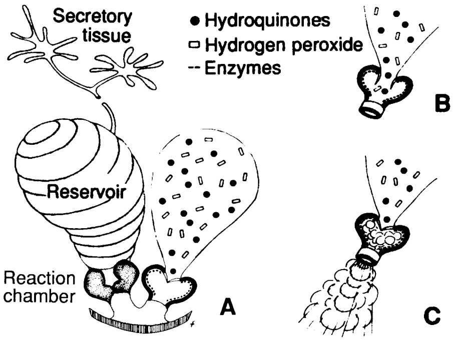

Fig. 2. Mode of operation of the bombardier beetle's glandular apparatus. (**A**) The pair of glands, with compartments of one gland cut open. (**B**) Intake phase, when chemical precursors from the reservoir are passed into the reaction chamber. (**C**) Exhaust phase, when the explosion in the reaction chamber causes an ejection of spray. During a discharge the sequence (A) → (B) → (C) is repeated several times, engendering the pulsed emission that characterizes the discharges.

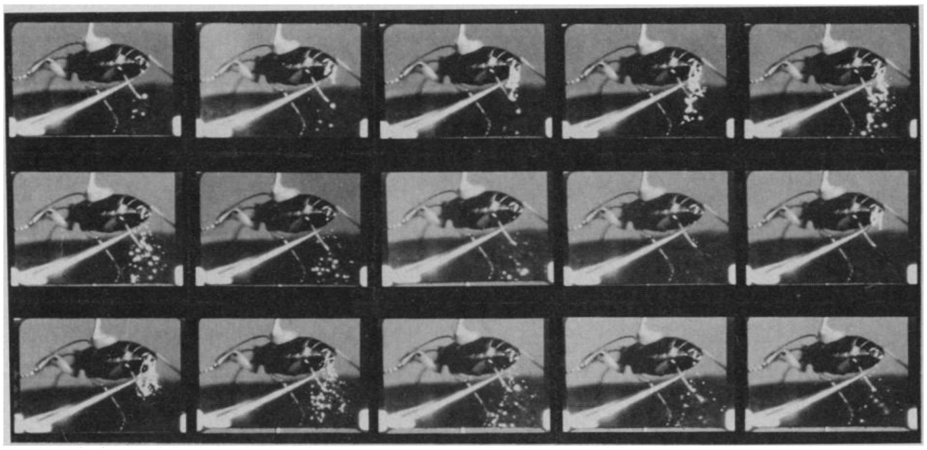

Fig. 4. Section of motion picture film of bombardier beetle discharge (4000 frames per second, proceeding horizontally from upper left to lower right), spanning 3.5 ms, and covering two pulsations. The beetle was tethered to a wire and was being pinched with forceps, as in Fig. 1A.

primitive bombardier beetle, the ozaenine *Goniotropis nicaraguensis*, which discharges its hot quinones as an unpulsed stream (*14*).

We postulate that the individual pulsations represent individual microexplosions, repeated one after the other as the beetle delivers its spray. Critical to the operation of such a cyclic mechanism is the maintenance of continuous pressure on the reservoir through sustained contraction of its musculature and an oscillatory opening and closing of the valve that controls access to the reaction chamber. We envision this valve oscillation to proceed passively. At the outset of events leading to an ejection, pressure from the reservoir overcomes the passive occlusory force of the valve, causing fluid to flow into the reaction chamber. This leads to a quick buildup of pressure in the chamber (as a consequence of both the oxygen liberated from hydrogen peroxide and the temperature increase) (*5*) with the result that the valve is forced closed. As pressure continues to build up in the chamber, a point is reached at which the chamber vents itself, shooting out its contents. With the chamber again below the feeding pressure of the reservoir, the cycle is reinitiated [and proceeds as diagrammed in Fig. 2: (A) → (B) → (C)]. Preliminary structural work shows the valve to be a one-way conduit, with an exit port projecting into the reaction chamber and guarded by what are essentially compressible lips (*15*). The oscillatory mechanism is thus virtually automatic. To effect an ejection, the beetle needs to control only the duration of compression of the reservoir, which it could achieve by conventional neuromuscular action.

From an adaptive point of view, a pulsed delivery system offers several advantages over a continuous discharge mechanism. First, it provides for a high discharge velocity without requiring muscles to supply the necessary pressure. Precursors can be supplied at low pressure; the chemical reaction generates the high pressure for propelling the discharge. The second advantage, related to the first, concerns the separation of control and propulsion functions. Muscle force shows low-pass characteristics; providing high forces generally involves a reduction in the precision of temporal control (*16*). Because the bombardier beetle does not use muscles to provide propulsion, the control function can be more accurate: short discharges can be produced without reduction in spray velocity. Spray delivery can thus be maintained constant over time, with the length of the pulse train adjusted to the magnitude and duration of an attack. Finally, the discontinuity of the reaction, inasmuch as it would provide for repetitive cooling of the reaction chamber through periodic introduction of reactants, could protect the enzymes from thermal denaturation.

A striking technological analog of the bombardier beetle is provided by the notorious V-1 "buzz" bomb of World War II (*17*). Both the beetle and the V-1 engender a pulsed jet through an intermittent chemical reaction, and both have passively oscillating valves controlling access to their reaction chambers. For a propelled vehicle such a system is suboptimal because thrust is discontinuous. For the bombardier beetle the appropriate measure is not thrust but rather production of an effective deterrent with good control and high discharge velocity, with investment of minimal muscular force. For this purpose the pulsed mechanism is ideal.

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7. We caused tethered beetles to discharge by pinching individual legs with forceps (Fig. 1A). The recording system consisted of a microphone (±12 dB from 1 to 100 kHz with a sensitivity of 26 μV/μbar at 4 kHz), positioned at 2.5 cm above the abdominal tip of the beetle; an amplifier (model 255 low noise amplifier, Ithaco); and a recorder (Lockheed magnetic tape recorder, model 417D; tape speed = 30 inches per second).
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11. We again induced tethered beetles to discharge by pinching individual legs with forceps (Fig. 1A). The acoustical detection system was as described (7). The piezoelectric crystal was buffered (Picometric amplifier model 181, Instrumentation Laboratory, Inc.) and amplified (model 255 low noise amplifier, Ithaco). Both microphone and crystal outputs were recorded at 15 inches per second (Lockheed magnetic tape recorder, model 417D). The crystal was positioned 0.5 to 0.75 cm from the abdominal tip of the beetle, along the anticipated trajectory of the spray (the line from the abdominal tip to the site on the beetle's leg pinched with forceps).
12. The speed (in frames per second) was set by the repetition rate of stroboscopic flashes used for illumination.
13. The velocity was calculated from tracings of the advancing spray front, as depicted in enlarged projections of the first two film frames of individual pulses.
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Electrophoresis of Flexible Macromolecules: Evidence for a New Mode of Transport in Gels

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Movement of macromolecules through low concentration agarose gels was investigated with linear poly(styrenesulfonate), linear DNA, star-shaped poly(styrenesulfonate), and circular DNA. Mobilities of weakly entangled flexible macromolecules were independent of molecular radius; within a homologous chemical sequence, electrophoretic separation at low field strengths depended solely on the degree of polymerization. These observations cannot be explained either by sieving or by reptation mechanisms; transport was apparently controlled by spatial variations of chain configurational entropy. Only when the chain was highly entangled did chain topology affect mobility. Evidence for entropically regulated transport clarifies how gel electrophoresis separates flexible macromolecules.

ALTHOUGH GEL ELECTROPHORESIS IS invaluable for fractionating biopolymers, the molecular mechanisms by which separation occurs are still not well understood. Chain entanglement plays a prominent role; thus, we defined three entanglement regimes for a relaxed, flexible macromolecule surrounded by a random gel (Fig. 1). A chain is unentangled when its mean

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