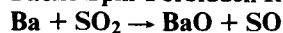


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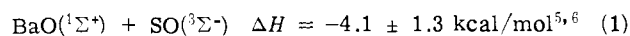
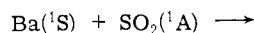
Facile Spin-Forbidden Reactions.



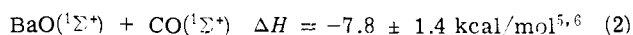
Sir:

Violation of the electron spin conservation rule¹ during a collision is rare but not unknown. Among the few fast spin-forbidden processes in the gas phase are the ion-molecule reaction² $\text{O}^+ (^4\text{S}) + \text{CO}_2 (^1\Sigma^+) \rightarrow \text{O}_2^+ (^2\Pi) + \text{CO} (^1\Sigma^+)$ and the quenching³ of $\text{O} (^1\text{D})$ by Xe or N₂. In condensed media, several examples of singlet to triplet conversion are reported in photochemical studies of organic molecules, for example, the fragmentation of tetramethyl-1,2-dioxetane and the isomerization of naphthalene.⁴

We have used laser-induced fluorescence to examine a spin-forbidden, gas-phase, neutral-neutral reaction



Insufficient energy is available for the spin-allowed production of excited $\text{SO}(a^1\Delta)$ ($\Delta H = 13 \text{ kcal/mol}$).⁷ The rate of eq 1 is large,⁸ by our measurements four times that of the spin-allowed reaction



despite comparable exothermicities. This observation may be explained by an electron jump mechanism.

The basic apparatus^{6,9} is shown schematically in Figure 1. A beam of Ba formed at 860° in the oven chamber reacts with thermal SO₂ gas (10⁻⁴ Torr) in the scattering chamber, under single-collision conditions. A pulsed, tunable dye laser beam, intersecting the Ba beam at right angles, excites a particular vibrational-rotational level of the BaO product. The population of this level can be determined from the intensity of the fluorescence, detected by a photomultiplier mounted beneath the Ba beam-laser beam intersection. We use the dye CSA-22¹⁰ to excite the (5,0), (6,0), (7,1), and (7,2) bands of the BaO (A¹Σ⁺-X¹Σ⁺) system.¹¹

Figure 2a shows data from part of a scan of the (5,0) band, from which the rotational populations of BaO (ν = 0) in Figure 2b are derived. The vibrational populations are

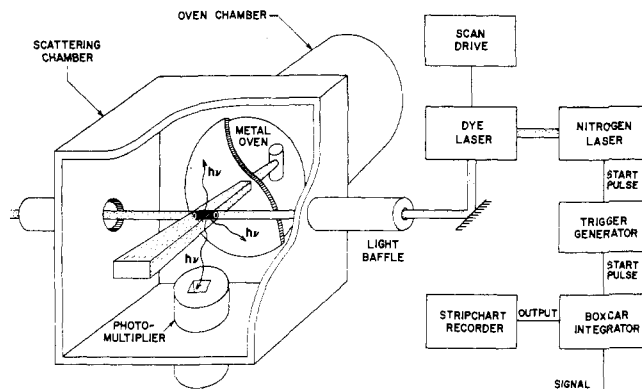


Figure 1. Schematic of the laser-induced fluorescence apparatus.

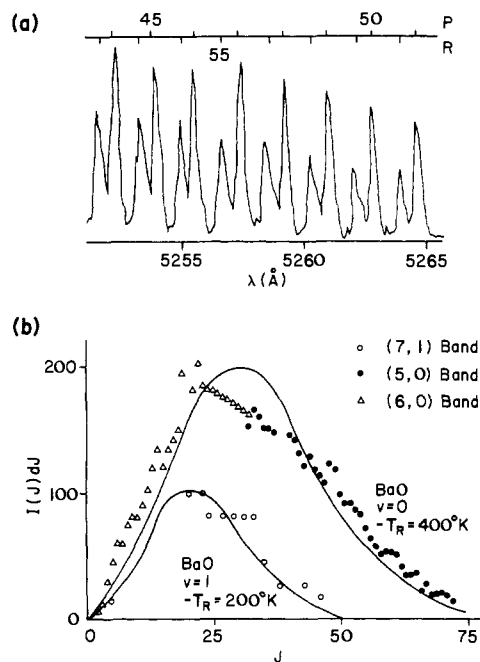


Figure 2. (a) A portion of the laser-induced fluorescence spectrum of BaO (ν = 0), from a scan of the BaO (A-X) (5, 0) band. The individual rotational lines are labeled. (b) Rotational populations of the BaO product, with the best fitting Boltzmann distributions. The ν = 1 values are properly scaled to those for ν = 0. The intensity scale is arbitrary.

$\nu_0:\nu_1:\nu_2 = 76:24:<4$ (no ν = 2 was observed). Of the initial relative kinetic energy (~1.1 kcal/mol) and reaction exothermicity, $4.6 \pm 1.6 \text{ kcal/mol}$ of the energy, on the average, remains for product translation and SO vibrational or rotational energy. This markedly asymmetric distribution of energy indicates a direct reaction mechanism, in agreement with the highly forward peaked angular distribution of BaO reported previously.⁸

Figure 3 shows cuts of relevant Ba-SO₂ surfaces and suggests a possible reaction mechanism. The reaction begins with the familiar electron-jump or harpoon mechanism.¹² The crossing of the ionic and neutral surfaces occurs at ~3.5 Å.¹³ The ion pair of the doublet species Ba⁺ and SO₂⁻ correlates with singlet and triplet states of Ba-SO₂, which are split in energy by an exchange integral. At large distances, this integral is small and the two states of the diradical are nearly degenerate. Thus transitions to the triplet surface may be accomplished by spin-orbit¹⁴ or spin-rotation coupling, following the electron jump. This coupling may be appreciable at large distances where the states are nearly degenerate, for in first-order perturbation theory

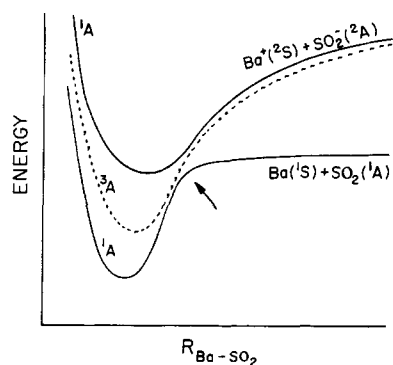


Figure 3. Sketch of a cut through the relevant Ba-SO₂ potential surfaces, along the Ba-SO₂ axis. The avoided crossing is marked by an arrow, and the triplet surface (dashed line) correlates to the reaction products along an alternate cut through the surface.

the energy dependent denominator of the coupling term is small. Reaction may then proceed in a straightforward manner on the triplet surface.

Although reaction 2 is not spin forbidden, it is slower than reaction 1 because the electron-jump mechanism cannot take place at large distances. The CO₂⁻ ion is isoelectronic with NO₂; hence its ground state is predicted to be bent, while CO₂ is linear. By virtue of the Franck-Condon principle, the vertical electron affinity of the molecule is negative,¹⁵ and hence the electron-jump mechanism cannot occur.

We hypothesize that an analogous electron jump mechanism accounts for the fast spin-forbidden O⁺ + CO₂ reaction. A near-resonant charge transfer may occur as the reactants approach at large distances. Following the electron jump, the system is on the quartet surface of the CO₂⁺(²Σ) + O(³P) configuration. This configuration also produces a doublet surface which correlates to the O₂⁺ + CO products and is nearly degenerate with the quartet at large distances. These two states mix as in reaction 1, and

the spin-forbidden step required for the reaction is accomplished.

Possible violation of the Wigner spin conservation rule should also be considered for other reactions if: (1) a long range electron jump is possible, (2) this gives rise to degenerate states of differing multiplicities, and (3) the state of different multiplicity correlates with exoergic product formation.

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