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SELECTIVE QUENCHING OF THE TWO PHOTOREACTION MODES OF RH(INH3)5B--ETC(U)
MAY 80 M T LARSON, A W ADAMSON, R C RUMFELDT N00014-76-C-0548
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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER

(14) TR-10

2. GOVT ACCESSION NO.

AD-A084340

3. RECIPIENT'S CATALOG NUMBER

(9)

4. TITLE (and Subtitle)

Selective Quenching of the Two Photoreaction
Modes of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$

5. TYPE OF REPORT & PERIOD COVERED

Technical Report, 1980

6. PERFORMING ORG. REPORT NUMBER

8. CONTRACT OR GRANT NUMBER(s)

(15) N00014-76-C-0548

9. PERFORMING ORGANIZATION NAME AND ADDRESS

University of Southern California
Department of Chemistry
Los Angeles, California 9000710. PROGRAM ELEMENT, PROJECT, TASK
AREA & WORK UNIT NUMBERS

NR 051-609

11. CONTROLLING OFFICE NAME AND ADDRESS

Office Of Naval Research (Code 472)
Arlington, VA 22217

12. REPORT DATE

(11) May 1980

13. NUMBER OF PAGES

12

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

(12) 17
Unclassified15a. DECLASSIFICATION/DOWNGRADING
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Rhodium Complexes
Bromopentaamminerhodium(III)
Photochemistry
Emission

Quenching

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See manuscript.

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Selective Quenching of the Two Photoreaction Modes of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$

by

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Prepared for Publication

in the

Journal of the American Chemical Society

May 7, 1980

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Abstract

$\text{Rh}(\text{NH}_3)_5\text{Br}^{(2+)}$ is known to emit in aqueous solution, and quenching of this emission by hydroxide ion is reported. The quenching obeys Stern-Volmer kinetics with a bimolecular quenching rate constant, k_q , of $2.7 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 5 °C. In acid solution the lifetime is 24.1 ± 0.1 nsec at 5 °C, with a temperature dependence of about 5 kcal/mole. The photochemistry is known to be primarily one of ammonia aquation, with a 10% component of bromide aquation. Under the same conditions as for emission lifetime quenching, there is parallel quenching of the ammonia aquation, with essentially the same k_q , but no quenching of the bromide aquation. It is therefore concluded that the emitting state is implicated in the former, but not in the latter. Possible revisions of excited state schemes to accommodate the new results are explored. $\leftarrow$

$2.7 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$

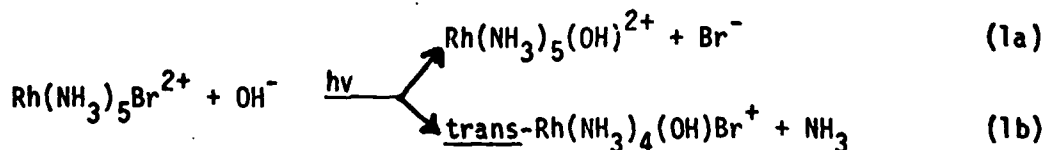
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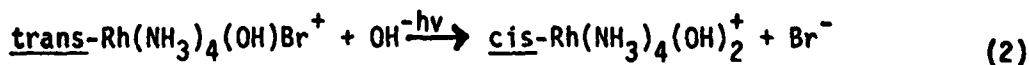
We report here what appears to be the first case of selective quenching of photochemistry of a d^6 complex, a Rh(III) ammine. Previous work from this Laboratory showed that the emission and the photochemistry for aqueous $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ are quenched almost completely in parallel by hydroxide ion.¹ The implication is that chemical reaction occurs from or via the emitting state, assumed to be the first thexi triplet state ($^3T_{1g}$ in O_h symmetry, or 3E or 3A_2 in C_{4v} symmetry). Chloride aquation is the only photoreaction mode for this complex, and it was of interest to extend the studies to $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$, which shows both ammonia and bromide aquation, the room temperature yields being $\phi_{\text{NH}_3} = 0.17-0.18$, and $\phi_{\text{Br}} = 0.019$.² Preliminary work has shown that the complex does emit in aqueous solution, and that the emission is quenchable by hydroxide ion.³

We report here an emission lifetime, τ , for $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ of 24.1 ± 1.2 nsec in 0.01 M perchloric acid at 5 °C, with a temperature dependence of about 5.1 kcal mole⁻¹.⁴ These values agree well with literature ones.⁷ Lifetime quenching by hydroxide ion obeys Stern-Volmer kinetics, as shown in Figure 1, giving a bimolecular quenching rate constant, k_q , of $2.7 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 5 °C, a value essentially at the diffusion limit.

In alkaline solution, the primary photochemistry is:



A complication is the photosensitivity of one of the products,⁸



We obtained relative values for ϕ_{NH_3} by following the absorbance change at an isosbestic wavelength for the two species of Eq. (2).⁹ Ammonia photoaquation is quenched by hydroxide ion, as shown in Figure 1, and the data give $k_q = 2.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 5 °C, in good agreement with the value from lifetime quenching. Reaction (1b) therefore occurs from or via the emitting state.

Reaction (1a), the minor pathway, is not adequately reflected in absorption spectral changes. We therefore determined the released Br^- ion independently, using a specific ion electrode.¹⁰ Within experimental error, there is no hydroxide quenching of ϕ_{Br} up to a hydroxide ion concentration as high as 0.01 M, at which level τ^0/τ would be 7.5 (see Figure 1). The conclusion is that the emitting state is not involved in the path for reaction (1a).

We now examine some of the implications of these results in the context of other work on the system. Kelly and Endicott² found efficient sensitization by triplet state biacetyl, concluding that therefore a $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ triplet state, designated " ^3X ", was produced. In addition, however, ϕ_{NH_3} showed a 2.8 kcal mole⁻¹ temperature dependence, while ϕ_{Br} was more nearly temperature independent. The observations called for a second state, " ^3Y ". The results could be accounted for if ^3X led only to ammonia aquation and lay 2.8 kcal above ^3Y , which led only to bromide aquation. It is necessary in this scheme that ^3X and ^3Y be in steady state equilibrium.

The above scheme encounters difficulties from our results. The emission presumably occurs from either ^3X or ^3Y , yet if this were so, bromide aquation would be quenchable along with the emission, contrary to observation. Alternatively put, since the two states are in steady state

equilibrium, quenching of ammonia aquation should require quenching of bromide aquation, contrary to observation.

An alternative two triplet state scheme is shown in Figure 2. Assuming applicability of ligand field theory for tetragonal geometry, excitation leads, after intersystem crossing, to 3E and 3A_2 thexi states. The former should be the lower in energy, and is assumed to give rise both to emission and to ammonia aquation. The temperature dependence of ϕ_{NH_3} is not large, and could just be the accidental net of the temperature dependencies of non-radiative and chemical reaction rates. The 3A_2 state undergoes bromide aquation (in competition with conversion to 3E); to accommodate the results, it is also the state populated in biacetyl sensitization. However, the orbital population of $^3A_2^{11}$ provides $d_{x^2-y^2}$ antibonding electron density, and it is difficult to see how this should lead to bromide labilization. A rationalization is the following. If we consider the geometries of the states, perhaps that of 3A_2 is relatively close to the ground state geometry (while 3E is highly distorted, as evidenced by the large Stokes' shift¹³). Facile relaxation of 3A_2 into the ground state manifold would produce a vibrationally "hot" molecule, leading to reaction by the normal thermal path, which is bromide aquation.

To explain the results with $Rh(NH_3)_5Cl^{2+}$, the ordering of the triplet levels could be inverted, or the photochemistry of 3E could now be made one of chloride aquation. Both maneuvers seem awkward. The emission from $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$ are quite similar in lifetime, temperature dependence, and spectrum.¹³ The emitting state thus appears to be of the same species in the two cases, suggesting that no change in ordering occurs. Possible change in reaction mode has indeed been rationalized qualitatively in terms of ligand field arguments,¹² to make the scheme of

Figure 2 acceptable. However, it seems awkward to have to assume that such reactivity change is not accompanied by a comparable degree of change in emission properties.

There is another, albeit more complicated, possibility. The emitting state, again taken to be a triplet, which we now call T_1° ,¹⁴ does not itself undergo chemical reaction, but generates one or the other reactive state by internal conversion. Ammonia aquation can occur through a second triplet state, T_2° , and halide aquation, through a quintet state, Q_1° .¹⁵ With a nearly uniform d-orbital occupancy, Q_1° might be less distorted from the ground state than the singlet and triplet thexi states, and therefore more apt to resemble the ground state in thermal reactivity (or to relax to a reactive hot ground state). One now accounts for the varying photochemistry in the $Rh(NH_3)_5X^{2+}$ series by supposing that while the T_1° energy does not vary much, those of Q_1° and T_2° relative to T_1° do vary sufficiently to vary the state populated via T_1° . Some direct crossing to Q_1° provides the bromide yield (and perhaps the 15% unquenchable portion of the chloride yield¹).

There are similarities to the d^3 system. There seems to be little doubt now that reaction can occur from either the first doublet or the first quartet thexi state of Cr(III) complexes.¹⁷⁻²⁰ In the case of the $Cr(NH_3)_5X^{2+}$ family, the same two reaction modes occur as with $Rh(NH_3)_5X^{2+}$, and we have in fact postulated that the doublet state tends to show the thermal reaction mode (analogous to Q_1°), and the quartet state, to obey the photolysis rules (analogous to T_2°).²⁰⁻²² Some of the same approaches used in the d^3 cases (see Refs. 17 and 19 especially) may prove to be useful in evaluating excited state schemes for Rh(III) amines.

Acknowledgement

This investigation has been support in part by grants from the U.S. National Science Foundation and from the U.S. Office of Naval Research.

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- (3) Larson, M.; Adamson, A. W. Abstracts, 178th ACS National Meeting, Washington, D. C., September 11, 1979.
- (4) $[\text{Rh}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ was prepared from $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{Cl})_2$ (Alfa Inorganics) according to published procedures.⁵ Lifetimes were measured using the 5 nsec pulse of a Nd glass laser described in Ref. 6.
- (5) Bushnell, G. W.; Lalor, G. C.; Moelwyn-Hughes, E. A. *J. Chem. Soc. A* 1966, 719.
- (6) (a) Adamson, A. W.; Walters, R. T.; Fukuda, R.; Gutierrez, A. R. *J. Am. Chem. Soc.* 1978, 100, 5241. (b) Gutierrez, A. R.; Adamson, A. W. *J. Phys. Chem.* 1978, 82, 902.
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- (8) Skipsted, L. H.; Ford, P. C. Private Communication (confirmed in our studies).
- (9) This isosbestic, at 361 nm, was determined by photolyzing to completion a solution of $\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$ in acid solution, making it alkaline so as to form trans- $\text{Rh}(\text{NH}_3)_4(\text{OH})\text{Br}^{2+}$, and then photolyzing this solution. We take the product to be cis- $\text{Rh}(\text{NH}_3)_4(\text{OH})_2^+$.⁸
- (10) After each increment of photolysis, the potential was measured using an Orion bromide electrode. The single junction calomel reference cell was isolated from the sample solution by means of a 5% agar-agar salt

bridge. All solutions were 0.2 M in sodium perchlorate as supporting electrolyte. The data were plotted as $\exp[(E_0 - E_t)/\alpha] - 1$ vs. time, $\alpha = RT/\beta$. The slope of such a plot is proportional to ϕ_{Br} for constant irradiation conditions.

- (11) The wave functions for the T_{1g} state, on reduction to tetragonal symmetry are: (Ref 12 and Griffith, J. S., "The Theory of Transition Metal Ions," Cambridge Press, 1961, Table A20, Appendix 2).

$$\begin{aligned} {}^{1,3}E: & -(\sqrt{3}/2)[(xy)^2(sz)^2(yz)^1(z^2)^1] - (1/2)[(xy)^2(xz)^2(yz)^1(x^2-y^2)^1]; \\ & +(\sqrt{3}/2)[(xy)^2(xz)^1(yz)^2(z^2)^1] - (1/2)[(xy)^2(xz)^1(yz)^2(x^2-y^2)^1] \\ {}^{1,3}A_2: & [(xy)^1(xz)^2(yz)^2(x^2-y^2)^1] \end{aligned}$$

- (12) Zink; J. I. Inorg. Chem. 1973, 12, 1018.
- (13) Thomas, T. R.; Crosby, G. A. J. Mol. Spec. 1971, 38, 118.
- (14) We prefer to use spin rather than orbital symmetry labels, the superscript zero denoting thermally equilibrated. The reason is that while distortion accompanying thermal equilibration could remain within the octahedral framework, e.g. tetragonal, it need not. One or more of the thexi states could, for example, have pentagonal symmetry or be triangularly prismatic. The matter of excited state geometry is as yet a rather obscure one.
- (15) The quintet state is not necessarily too high in energy to be considered. Qualitatively, while two electrons are promoted, two spin pairing energies are recouped. In fact, possible parameters in tetragonal geometry can place 5T_2 between the 3E and 3A_2 states of T_{1g} parentage.¹⁶
- (16) Konig, E; Kremer, S. "Ligand Field Energy Diagrams," Plenum Press, New York, 1977.
- (17) See Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Sostero, S.; Traverso, O. J. Chem. Soc. Faraday I 1980, 76, 162 and references therein.

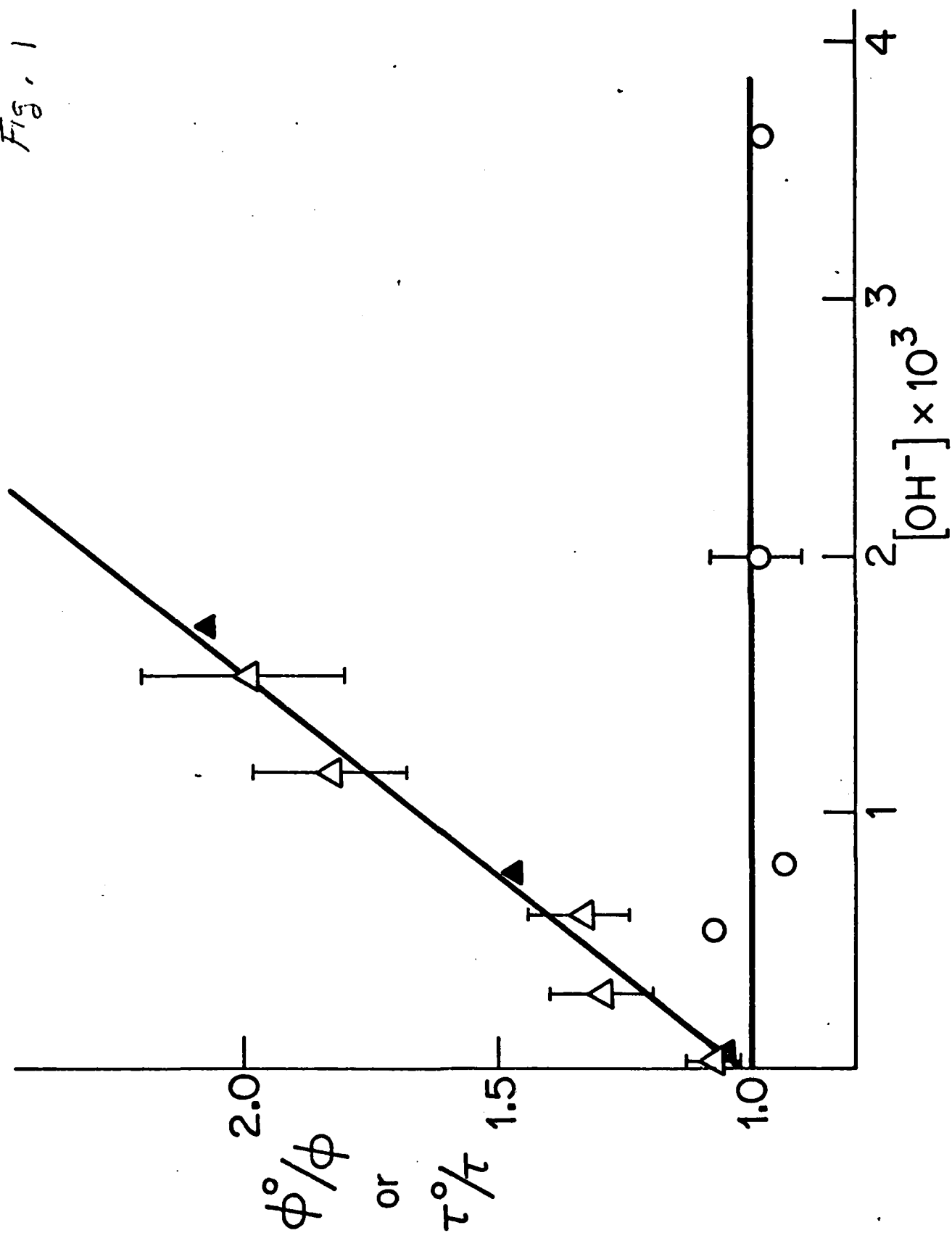
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Legends for the Figures

Figure 1. Stern-Volmer plot of hydroxide ion quenching of excited state processes of aqueous $\text{Rh}(\text{NH})\text{Br}^{2+}$ at 5 °C. Δ , Ammonia aquation, Δ , emission, O, bromide aquation.

Figure 2. Schematic two-state energy scheme, the abscissa indicating degree of distortion, and light parallel lines denoting vibrational states.

Fig. 1



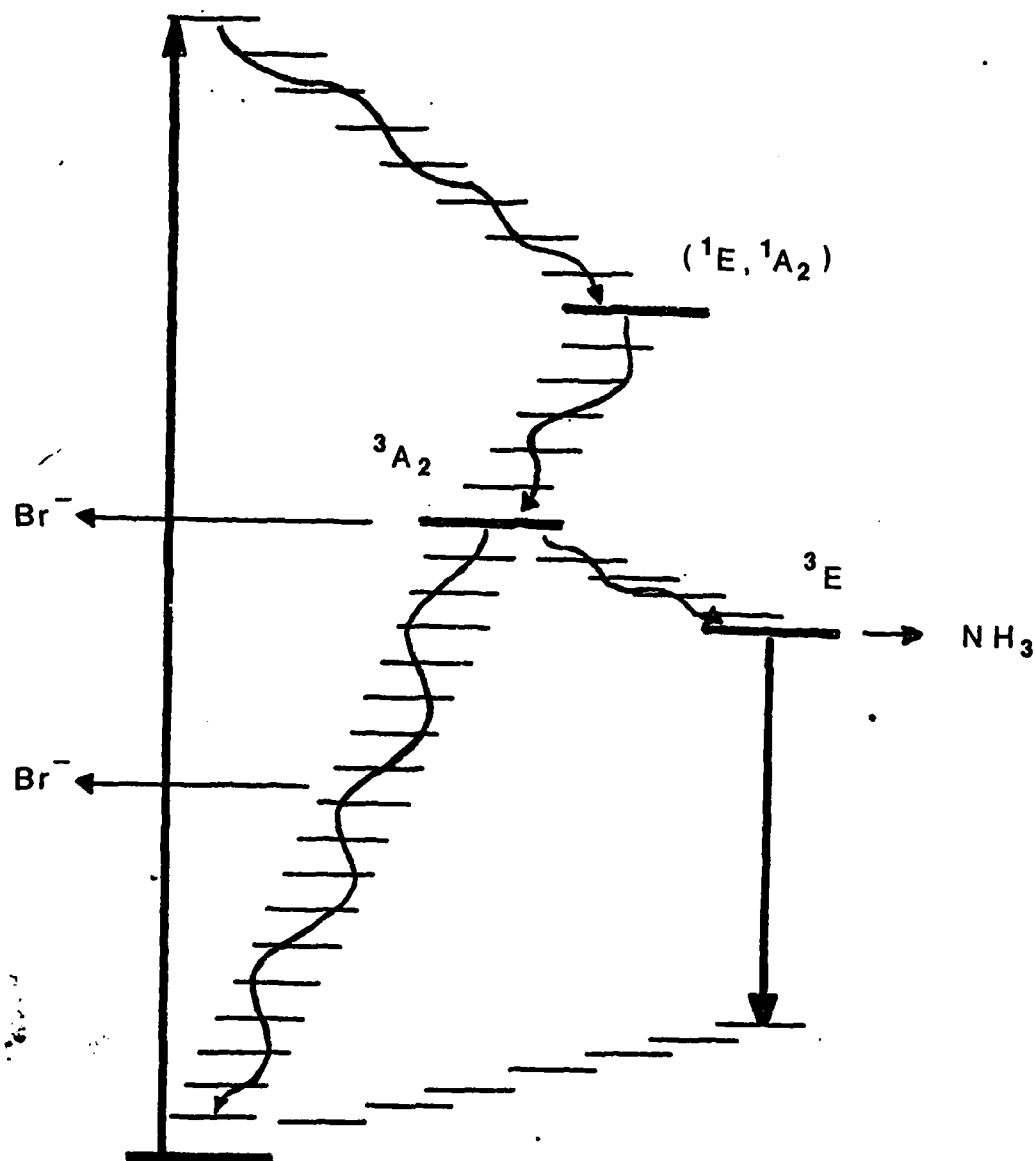


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