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Dissociative excitation of HgBr_2 in collisions with a beam of metastable nitrogen

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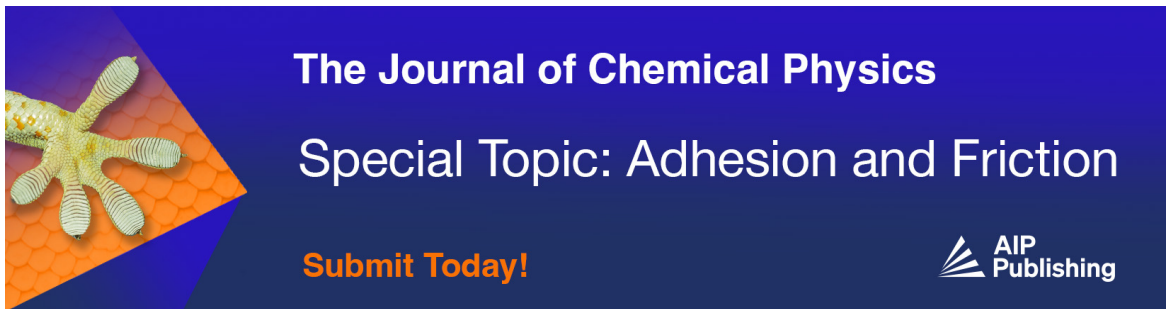


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ment was confirmed by the observation of phosphorescence of CuPc and ZnPc around 900–1200 nm at liquid He temperature.⁷ The close similarity of the spectra in Fig. 1 to those in the earlier studies suggests that the present photoelectrochemical response also arises from $S-T$ excitation.

Bubbling of oxygen in place of argon led to a significant decrease in the photocurrent; this is attributable to quenching of the triplet excited state of CuPc by oxygen. A visible photocurrent (at 630 nm) in the same experimental system was also diminished by oxygen to the same extent as the NIR one. This implies that, in the case of the visible photocurrent, charge transfer to an unknown acceptor occurs mostly via intersystem crossing to the triplet state.

The significance of the present study can be summarized as follows. (1) The finding of the NIR photocurrent in the electrochemical system demonstrates the utility of NIR light as an exciting source in the field of dye photoelectrochemistry. (2) The mechanism of visible photocurrent generation can be inferred by comparing its behaviors with those of the NIR photocurrent, as mentioned in the preceding paragraph. (3) The present method provides a novel means of determining the position of triplet states. For that purpose, the measurement of phosphorescence or $S-T$ absorption has been of use as a conventional technique. However, in most cases phosphorescence can be detected only at extremely low temperature. $S-T$ absorption has been applicable to only a few materials. The present method is superior to them, in that it is available at ordinary temperature, and that the NIR structure was far more sensitively detected by our method than by $S-T$ absorption.

NIR light can be used in the study of semiconductor electrode-dye solution systems. The spectrum of the NIR sensitized photocurrent in this case would contribute to locating the triplet state of a dissolved dye molecule; this would be of great use in the field of photochemistry. Presumably, the present method may be made applicable to molecules free from heavy atoms by some experimental modifications, e.g., the use of a strong NIR light source or the improvement of the SN ratio of the measuring apparatus. An alternative way is addition of a molecule containing a heavy atom, as is conventional with $S-T$ absorption. The scope of the applicability of the method should be extensively examined hereafter.

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Dissociative excitation of HgBr_2 in collisions with a beam of metastable nitrogen^{a)}

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The mercuric halide compounds HgBr_2 , HgCl_2 , and HgI_2 have been of recent interest because of laser output achieved on the $B^2\Sigma-X^2\Sigma$ transition in the respective mercuric-halide radicals in the range of 400–600 nm. Population inversion has been achieved by photodissociation and electron impact excitation in mixtures of the mercuric-halide compounds and rare gases.^{1–8} Recently, Burnham has noted improved improved laser efficiency and output power when nitrogen gas has been added to the lasing mixture.⁸ The improved performance with added N_2 is likely due either to direct pumping of the upper laser level by excited states or to collisional dissociation of the ground state radical which prevents bottlenecking.

In this note we report the observation of $\text{HgBr}(B-X)$ fluorescence resulting from collisions of HgBr_2 with a vibrationally excited beam of nitrogen molecules in the $A^3\Sigma_u^+$ electronic state. The beam source used was a glow-discharge maintained in pure N_2 undergoing nozzle expansion.^{9,10} The most probable energy of the resulting beam was 180 meV and a lower limit on the flux value was determined to be 10^{14} atoms/s sr.

Previous studies with Cd and Zn target vapors, indicated that the beam was vibrationally excited N_2 in the $A^3\Sigma_u^+$ metastable state.¹⁰ The temperature of the vibrational distribution was determined to be near 4000 °K.

The HgBr_2 vapor was titrated into the beam path from

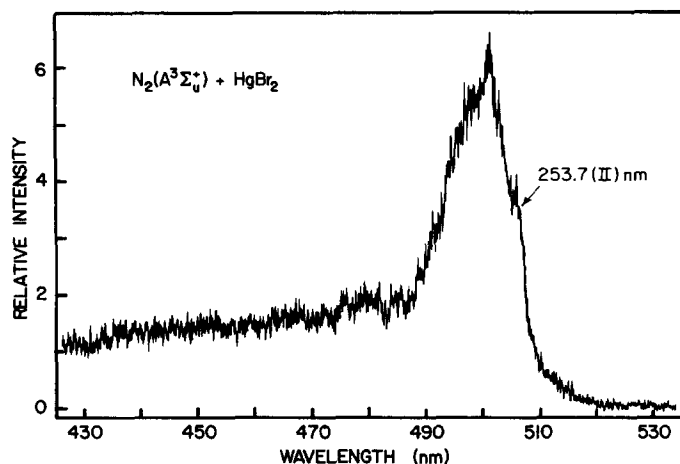


FIG. 1. Plot of relative intensity vs wavelength of the $\text{HgBr}(B-X)$ fluorescence resulting from collisions of $\text{N}_2(A^3\Sigma_u^+)$ with HgBr_2 . Monochromator resolution is 1.6 nm. Second order $\text{Hg}(6^3P)$ emission at 507.4 nm is also present in the spectrum as indicated.

a Pyrex reservoir heated by nichrome wire. The number density was estimated to be less than 10^{15} cm^{-3} in the 0.5 cm^3 interaction volume.¹¹ The interaction of the N_2 metastable beam with the target vapor was observed at 90° to the beam axis with a monochromator and cooled phototube.

For the HgBr_2 target, Fig. 1 shows the relative fluorescence observed in the range 430 to 530 nm for a monochromator resolution of 1.6 nm. The spectrum continues to decline in intensity without line structure to near 350 nm. The spectrum is in qualitative agreement with the spectrum of sidelight fluorescence from a HgBr_2 laser discharge.² The fluorescence is identified as the $B^2\Sigma-X^2\Sigma$ transition in HgBr by referring to studies by Wieland.¹² Laser output has been observed near the intensity maximum at 501.8 nm.

From such a fluorescence yield, it is clear that $\text{N}_2(A)$ can directly populate the upper laser level in HgBr by dissociative excitation of HgBr . Because of the small interaction volume and the low beam and target densities, the excitation here is under single-collision conditions and hence excludes a two-step process. Since we do not have an accurate line density of the target vapor, we could not determine an effective cross section for the HgBr dissociative excitation.

In addition to the HgBr fluorescence in Fig. 1, some $\text{Hg}(6^3P)$ emission appears in second order at 507.4 nm.

The observation of the first order line at 253.7 nm confirms this conclusion. The dissociation of HgBr_2 into $\text{Hg}(6^3P)$ and two bromine atoms requires $70\,189 \text{ cm}^{-1}$ which corresponds in energy to $v=18$ of the $\text{N}_2(A)$ state.^{12,13} The dissociation of HgBr_2 into $\text{Hg}(6^3P)$ and Br_2 requires $54\,411 \text{ cm}^{-1}$ which corresponds to $v=4$ of the $\text{N}_2(A)$ state. The excitation of the $\text{Hg}(6^3P)$ state from a single collision of $\text{N}_2(A)$ with HgBr_2 is therefore energetically possible. Emission from $\text{Hg}(7^3S)$ at 435.8 and 546.1 nm was not observed as it has been in discharge sidelight.² The dissociation of HgBr_2 into $\text{Hg}(7^3S)$ and Br_2 requires $77\,394 \text{ cm}^{-1}$ which corresponds to vibrational states with $v>23$. Since the $\text{N}_2(A)$ dissociation limit is near $79\,000 \text{ cm}^{-1}$, we do not expect to see 7^3S emission. The ratio of peak intensities of the HgBr broadband and the Hg line emission is somewhat higher than indicated in Fig. 1 due to the reduced phototube response at 500 nm.

In conclusion we have demonstrated that a vibrationally excited $\text{N}_2(A)$ beam dissociatively excites HgBr_2 producing in part $\text{HgBr}(B^2\Sigma^+)$. Without further study, one must assume that all vibrational levels of sufficient energy participate in this excitation. Further, we have inferred that certain vibrational levels can dissociatively excite HgBr_2 producing $\text{Hg}(6^3P)$. We expect that the same study made with HgCl_2 and HgI_2 will yield similar results.

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