

#187

# ANTI-STOKES PHOTOSENSITIZATION. CONCEPT AND DEMONSTRATION OF A "RED LIGHT" TO "BLUE LIGHT" TRANSFORMATION

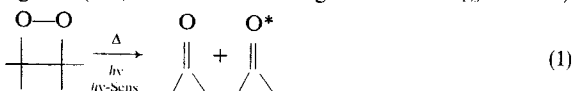
Nicholas J. Turro \*, David Brewer, William Farneth, and V. Ramamurthy

Chemistry Department, Columbia University  
New York, New York 10027. Received July 26, 1977.

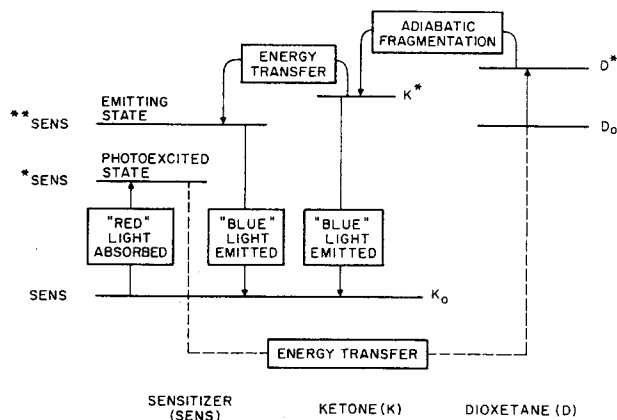
**ABSTRACT.** — We describe herein the concept and demonstration of a "red light to blue light" experiment in which absorbed "red photons" are transformed into "blue photons" via a strategy involving a series of steps, the most important of which are: 1) energy transfer from red light absorbing sensitizers to a dioxetane; 2) the adiabatic photoreaction of dioxetanes to produce excited carbonyl fragments; 3) emission of blue light by the excited carbonyl fragment and 4) an energy transfer to sensitizer states that emit blue light (Fig. 1). Experimental demonstrations of the red light to blue light concept are given for systems involving tetramethyl-1, 2-dioxetane as an energy store and various red light absorbing sensitizers.

## Introduction

Dioxetanes may be decomposed by thermal or photochemical excitation to produce electronically excited carbonyl fragments<sup>1</sup>. The latter are capable of transferring electronic energy to a variety of energy acceptors. The observation that the chemiluminescent decomposition of dioxetanes may be effected by energy transfer from triplet energy donors suggests an experimental means of converting absorbed "red" light into emitted "blue" light. The idea is as follows: a low energy photon,  $h\nu_R$  ("red" light) is absorbed by an energy donor (sensitizer) which is capable of causing decomposition of a dioxetane to produce an electronically excited carbonyl fragment (i. e., via electron exchange induced energy transfer).



The electronically excited carbonyl fragment in turn is capable of emitting high energy photons  $h\nu_B$  (blue light) or is capable of transferring energy to the energy donor (now in its ground state) to produce an electronic state of the donor. If this state emits at short wavelengths (in the "blue") a second pathway for effecting a "red" (absorbed) light to "blue" (emitted) light transformation is possible. The strategy for the red light to blue light experiment is outlined in Figure 1.



**Figure 1.** — Strategy for a red light to blue light experiment employing the photosensitized adiabatic fragmentation of a dioxetane as the key step in the uphill photosensitization. See text for discussion.

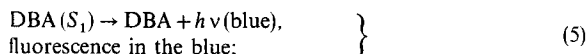
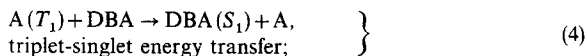
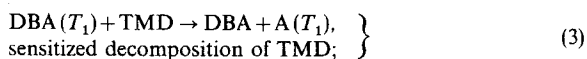
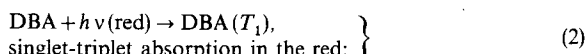
\* Address correspondence to this author.

Conceptually, the photosensitization process which produces an excited carbonyl fragment is an example of "chemical photon doubling" in the sense that the energy of the absorbed (red) photon is amplified (doubled) by extracting the necessary energy from the free energy of a chemical reaction.

We report here evidence that photosensitization and "red, light" to "blue light" transformations corresponding to the principle enunciated above can be experimentally achieved by use of tetramethyl-1, 2-dioxetane as an "energy amplifier". The systems studied involve (a)  $S_0 \rightarrow T_1$  (red light) excitation of the sensitizer followed by an eventual  $T_1$  (acetone)  $\rightarrow S_1$  (sensitizer) energy transfer and  $S_1$  (sensitizer)  $\rightarrow S_0$  + blue light (fluorescence) and (b)  $S_0 \rightarrow S_1$  (red light) excitation of the sensitizer followed by an eventual  $T_1$  (acetone)  $\rightarrow S_0$  + blue light (phosphorescence).

## The 9, 10-dibromoanthracene-dioxetane System

The 9, 10-dibromoanthracene (DBA)-tetramethyldioxetane (TMD) system possesses some especially favorable characteristics for a red light to blue light transformation via the steps indicated in equations 2-5. It has been shown that: (a) anthracene triplets ( $\sim 42$  kcal/mole) are capable of producing acetone triplets (78 kcal/mole) via photosensitized decomposition of TMD<sup>2</sup>; (b) DBA possesses a significant  $S_0 \rightarrow T_1$  absorption<sup>3</sup> and (c) "spin-forbidden" triplet singlet energy transfer from  $T_1$  (acetone) to  $S_0$  (DBA) is remarkably efficient ( $\Phi_T^T = 0.2-0.3$ )<sup>4</sup> (Fig. 2).



Experimental evidence for the occurrence of the above "red light to blue light" conversion in DBA-TMD system is given in Table I which compares the intensity of DBA fluorescence excited by a He/Ne laser under several conditions. In fact, excitation of solutions of DBA ( $\sim 10^{-1}$  M) and TMD ( $\sim 10^{-2}$  M) in  $N_2$  saturated benzene with He/Ne laser (632.7 nm) through a 500 nm cut-off filter leads to enhanced

Table I. — Emission intensity upon "red light" to "blue light" conversion

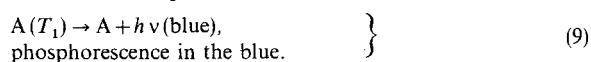
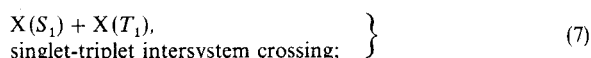
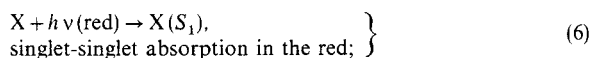
Solution <sup>a</sup> Conditions	Temp (°C)	$I_{\text{total}}$ <sup>b</sup>	$I_{\text{thermal}}$ <sup>c</sup>	$I_{\text{scatter}}$ <sup>d</sup>	$I_{\text{hv}}$ <sup>e</sup>
(i) aerated [DBA]=0.013 [TMD]=0.079	15 ± 0.5	7 300 ± 350	3 070 ± 150	1 590 ± 80	2 640 ± 580
(ii) N <sub>2</sub> bubbled [DBA] = 0.013 [TMD] = 0.079					
(iii) aerated <sup>f</sup> [DBA] = 0.013 [TMD] = 0.079	25 ± 0.5	18 510 ± 900	14 060 ± 750	1 550 ± 80	2 900 ± 1 730
(iv) N <sub>2</sub> bubbled [DBA] = 0.013 [TMD] = 0.079 [CN $\searrow$ C.N] = 0.01	15 ± 0.5	16 470 ± 800	1 530 ± 80	1 460 ± 80	13 840 ± 960

decomposition of TMD as determined by NMR or by chemiluminescence intensity. The emission spectrum observed during the photodecomposition of TMD is identical to that observed upon photoexcitation of a DBA solution. That the observed emission is not due to triplet-triplet annihilation of DBA <sup>3</sup> or two photon absorption by DBA is demonstrated by the reduced emission in the absence of TMD (see Table I). In the above system, acrylonitrile and *trans*-dicyanoethylene ( $E_T$ : 60-70 kcal/mole) are found to quench luminescence. This observation requires that some intermediate(s) along the red light to blue light pathway is being intercepted by that quencher. It was found that neither of these olefins quench  $S_1$  of DBA (~76 kcal/mole) under the reaction conditions. Because of the poor energy match, quenching of DBA by energy transfer would be expected to be very inefficient. Of the remaining candidates, we favor quenching of acetone triplets by

the cyanoethylenes by analogy to previous studies of the chain decomposition of TMD induced by photosensitizers <sup>5</sup>. The ability to quench acetone triplets by an external quencher requires that at least some triplets become free of the solvent cage before energy transfer to  $S_1$  of DBA occurs. This result is in agreement with previous studies <sup>2</sup>.

### The Xanthione-dioxetane System

A second example of redlight to blue light transformation is available in the xanthione (XT-TMD) system equations (6)-(9):



In this case, excitation of the  $S_0 \rightarrow S_1$  ( $n, \pi^*$ ) transition of XT ( $E_{S_1} = 44$  kcal/mole) is effected by red light (632.7 nm He/Ne laser) and blue light from acetone phosphorescence (420 nm) is observed. Figure 3 shows the pertinent energy diagram. The proposed cycle is quite analogous to that for the DBA-TMD system except that the major component of "blue" light is the phosphorescence from acetone. The latter can be quenched by  $O_2$ , acrylonitrile and crotonitrile. A minor component of the emission is apparently due to either  $S_1$  fluorescence of acetone or  $S_2$  fluorescence of XT <sup>6</sup>. This minor emission (15%) could not be quenched by  $O_2$ , acrylonitrile and crotonitrile. As the emission was very weak the unequivocal identification to one of those was not possible. When xanthione and TMD are excited (632.7 nm) in the presence of either diphenyl anthracene (Table III) or diphenylethylenyl anthracene blue emission of the anthracenes was readily observable (Fig. 4).

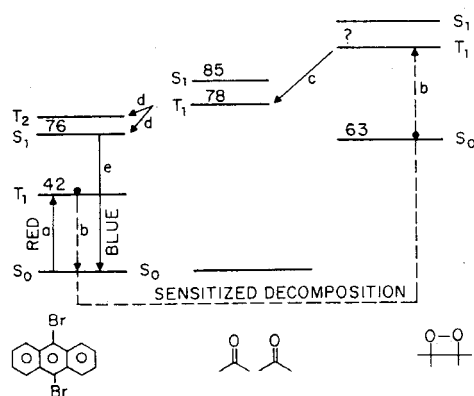


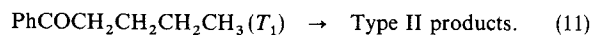
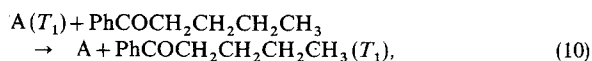
Figure 2. — Energy diagram showing the pathways for a red light to blue light conversion employing 9, 10-dibromoanthracene (DBA) as sensitizer. The energies refer to an arbitrary zero energy for molecules in their ground state, except for dioxetane which is placed at 63 kcal/mole, relative to the arbitrary zero, because this energy is released and available for electronic excitation.

Table II

Solution <sup>a</sup> Conditions	Temp. (°C)	$I_{\text{total}}^b$	$I_{\text{thermal}}^c$	$I_{\text{scatter}}^d$	$I_{h\nu}^e$
(v) N <sub>2</sub> bubbled [DBA] = 10 <sup>-3</sup> [XT] = 10 <sup>-4</sup> [TMD] = 10 <sup>-1</sup>	15 ± 0.5	83 500 ± 500	1 500 ± 50	200 ± 50	81 800 ± 600
(vi) O <sub>2</sub> bubbled [DBA] = 10 <sup>-3</sup> [XT] = 10 <sup>-4</sup> [TMD] = 10 <sup>-1</sup>					
(vii) N <sub>2</sub> bubbled [DBA] = 10 <sup>-3</sup> [XT] = 10 <sup>-4</sup> [TMD] = 10 <sup>-1</sup> [CN $\searrow$ $\swarrow$ CN] = 10 <sup>-2</sup>					

As in the DBA-TMD system, quenching results require that at least some triplet acetone escape the cage before energy transfer to the cage partner takes place. To further demonstrate this a three component system (valerophenone, XT, TMD) was studied in which a photochemical reaction occurs *via* energy transfer from acetone triplet.

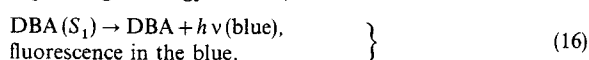
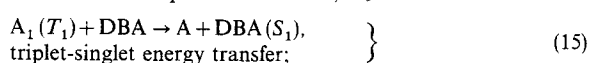
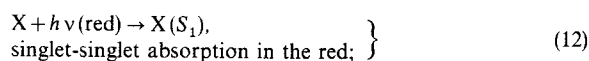
It has been shown previously that biacetyl ( $E_T = 55$  kcal/mole) could photosensitize formations of valerophenone triplets ( $E_T = 72$  kcal/mole) in the presence of TMD<sup>5c</sup>. Xanthione behaves similarly ( $E_T \sim 42$  kcal/mole). Thus, irradiation of the ternary system TMD (10<sup>-2</sup> M), XT (10<sup>-3</sup> M) and valerophenone (0.1 M) with He/Ne laser effects the type II reaction of valerophenone to produce acetophenone, as identified by NMR. In accordance with the previously described work we interpret this result to mean that the  $T_1$  of XT sensitizes the decomposition of TMD to produce *free*, acetone triplets which then transfer excitation to valerophenone triplets (Fig. 5). The latter then undergo type II reaction (equations 6-8, followed by equations 10 and 11):



#### The Xanthione, 9,10-dibromoanthracene and Tetramethyl dioxetane System

The "red" light to "blue" light conversion in the above two systems is inefficient due to either poor absorption by the sensitizer (DBA) or poor emission by the acceptor or emitter (XT) and acetone. The most efficient demonstration of a red light to blue light effect was found in the ternary system XT, DBA and TMD. Some results are shown in Table III.

This system is remarkable in its high efficiency in spite of its complexity. The overall red light (absorbed by xanthione to form  $S_1$ ) to blue light (emitted by  $S_1$  of DBA) transformation presumably involves: (a) intersystem crossing  $X(S_1) \rightarrow X(T_1)$ ; (b) energy transfer  $X(T_1) + \text{TMD} \rightarrow X + A(T_1)$ ; (c) energy transfer  $A(T_1) + \text{DBA} \rightarrow A + \text{DBA}(S_1)$  equations 12-16. The emission spectrum is shown in Figure 6:



In summary, we have demonstrated that TMD can be decomposed with red light absorbed by low energy sensitizers and the absorbed energy can be converted into "blue" light. In addition we have shown that excited acetone escapes the cage before energy transfer to the sensitizer can take place. It is generally assumed that the exothermic triplet-triplet energy transfer is diffusion limited in low viscosity organic solvents. However, it has already been shown<sup>7</sup> that exothermic triplet energy transfer is, in fact, less than diffusion controlled in some cases<sup>8</sup>. The unique feature of our experiments is that donor (acetone\*<sup>3</sup>) and acceptor (DBA) are produced already in the solvent cage. But it is clear from the quenching studies that acetone triplets can escape the solvent cage before energy transfer to DBA. This is unlikely to be due to the escape of dioxetane\* from the cage before the cleavage as the lifetime of dioxetane\* is estimated to be less than 10<sup>-11</sup> sec<sup>9</sup>. It is not clear whether the relatively slow rate of transfer is due to poor Franck-Condon factors prompted by the large energy gap between donor, e. g., (acetone, 78 kcal/mole) and acceptor (DBA, 42 kcal/mole), or whether electronic factors are important in determining the energy transfer rate constant.

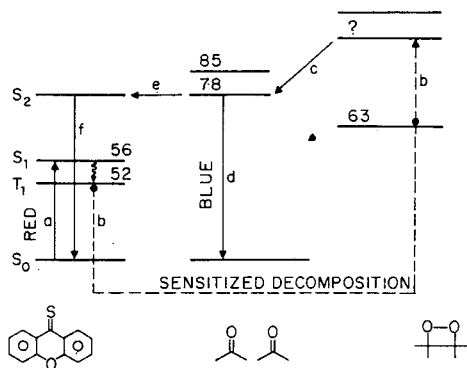
#### Experimental

Tetramethyl-1,2-dioxetane was prepared according to the literature procedure<sup>10</sup>. Xanthione was prepared from xanthone using phosphorous pentasulphide. Dibromoanthracene (Aldrich) was recrystallized from ethanol several times

Table III

Solution <sup>a</sup> Conditions	Temp. (°C)	$I_{\text{total}}^b$	$I_{\text{thermal}}^c$	$I_{\text{scatter}}^d$	$I_{\text{hv}}^e$
(viii) N <sub>2</sub> bubbled [DPA] = 10 <sup>-3</sup> [XT] = 10 <sup>-4</sup> [TMD] = 10 <sup>-1</sup>	15 ± 0.5	1 550 ± 50	60 ± 15	10 ± 5	1 480 ± 70
(ix) O <sub>2</sub> bubbled [DPA] = 10 <sup>-3</sup> [XT] = 10 <sup>-4</sup> [TMD] = 10 <sup>-1</sup>					

<sup>a</sup> All intensities are an integrated number of photon counts at 450 ± 10 nm over an arbitrary but uniform collection time. Each value is the average of 10-20 separate measurements. Errors represent the scatter in the data. <sup>b</sup>  $I_{\text{total}}$  = measured emission intensity with excitation at 632.7 through a 500 nm cut-off filter. <sup>c</sup>  $I_{\text{thermal}}$  = measured emission intensity with excitation source blocked. <sup>d</sup>  $I_{\text{scatter}}$  = measured intensity of a solution without TMD. <sup>e</sup>  $I_{\text{hv}} = I_{\text{T}} - (I_{\text{thermal}} + I_{\text{scatter}})$  = emission intensity due to a photochemical pathway. <sup>f</sup> data taken at different counting rate-normalized.

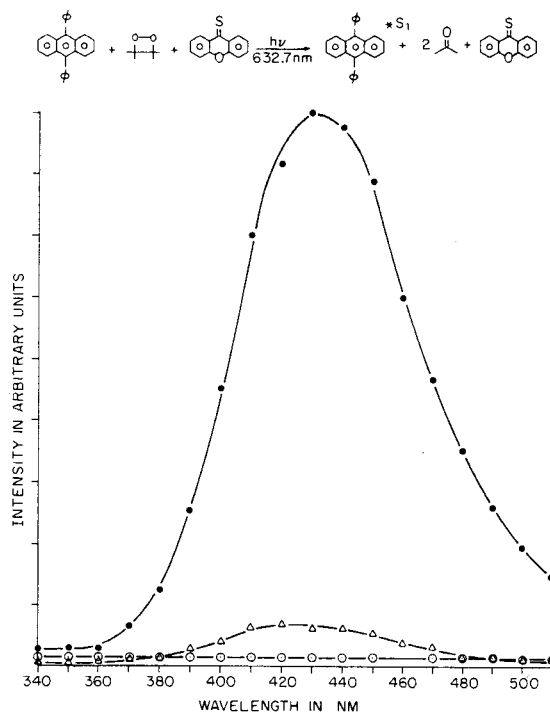


**Figure 3.** — Energy diagram showing the pathways for a red light to blue light conversion employing xanthione (XT) as sensitizer. The energies refer to an arbitrary zero energy for molecules in their ground state, except for diacetone which is placed at 63 kcal/mole, relative to the arbitrary zero, because this energy is released and available for electronic excitation.

before use. All quenchers used (acrylonitrile, crotononitrile and dicyanoethylene) were either distilled or recrystallized before use.

Excitation was conducted using a He/Ne laser (632.7 nm) and the emission was monitored at right angles using a system that included Ortec bin modules, a 0.25 M Jarell-Ash monochromator, EMI 983 QKA phototube and a Northern Econ NS 906 multichannel pulse height analyzer. Nitrogen, oxygen or air saturation (Tables) was accomplished by bubbling 3 ml solutions in a long necked cell equipped with teflon stopcocks for 300 sec.

Total emission constituted thermal decomposition of TMD, scatter and any other process in addition to the red light to blue light conversion. Correction was applied for the thermal process by measuring the light emission at the same temperature without excitation light on (He/Ne laser). Scatter and other processes were taken into account by exciting a solution of DBA without TMD.



**Figure 4.** — Emission spectrum of diphenyl anthracene upon red light to blue light conversion [DPA] = 10<sup>-3</sup> M; [XT] = 10<sup>-3</sup> M; [TMD] = 10<sup>-2</sup> M. ●, total emission (Thermal and Scatter included); ▲, thermal and Scatter; ○, scatter alone.

#### Acknowledgement

The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589) and the National Science Foundation (Grants CHE-76-18690 and NSF-CHE-74-04673) for their generous support of this research.

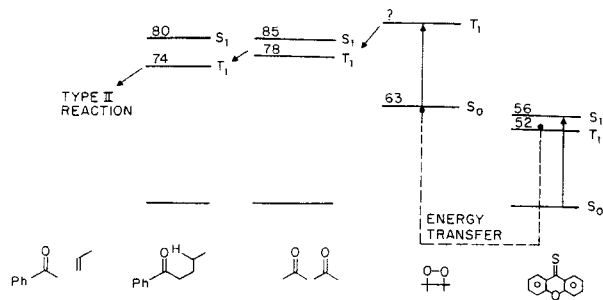


Figure 5. — Energy diagram showing the pathways for "uphill" photosensitization of the Type II reaction of valerophenone with xanthione as sensitizer.

## REFERENCES

- <sup>1</sup> N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H. C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974); N. J. Turro, and P. Lechtken, *Pure and Appl. Chem.*, **33**, 363 (1973). P. Lechtken, *Pure and Appl. Chem.*, **33**, 363 (1973).
- <sup>2</sup> C. S. Foote, and T. D. Darling, *Pure and Appl. Chem.*, **41**, 495 (1975).
- <sup>3</sup> S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).
- <sup>4</sup> N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H. C. Steinmetzer, and W. Adam, *J. Amer. Chem. Soc.*, **96**, 1627 (1974).
- <sup>5</sup> (a) W. J. Baron, and N. J. Turro, *Tetrahedron Letters*, 3515 (1974); (b) N. J. Turro, and W. H. Waddell, *Tetrahedron Letters*, 2069 (1975); (c) N. J. Turro, and P. Lechtken, *Tetrahedron Letters*, 565 (1973).
- <sup>6</sup> J. R. Huber, and M. Mahaney, *Chem. Phys. Lett.*, **30**, 410 (1975); M. Mahaney, and J. R. Huber, *Chem. Physics*, **9**, 371 (1975).
- <sup>7</sup> N. J. Turro, N. E. Schore, H. C. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **96**, 1936 (1974).

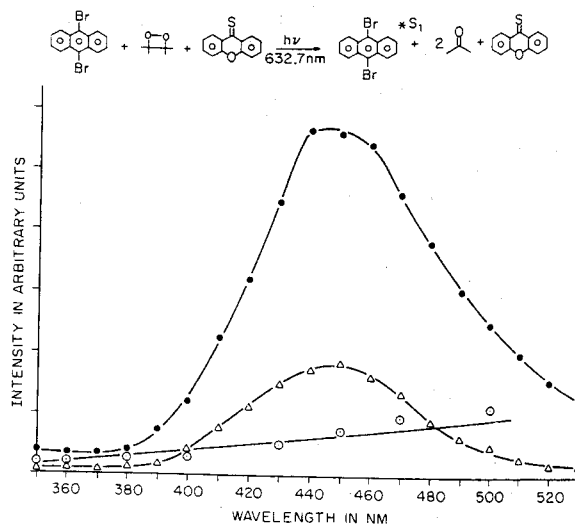


Figure 6. — Emission spectrum of dibromoanthracene upon red light to blue light conversion [DBA] =  $10^{-4}$  M; [XT] =  $10^{-3}$  M; [TMD] =  $10^{-2}$  M. ●, total emission (Thermal and Scatter included); △, thermal and Scatter; ○, scatter alone.

- <sup>8</sup> P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5715 (1967); P. J. Wagner, and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968); K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, **4**, 315 (1972).
- <sup>9</sup> K. K. Smith, Y. Y. Koo, G. B. Schuster, and K. J. Kaufmann, *Chem. Phys. Lett.*, **48**, 267 (1977).
- <sup>10</sup> K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J. Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975).