The second and apparently most important mechanism is an indirect effect involving changes in the chemical properties of the methyl group with deuterium substitution. It appears that the shortening of the C–D bond tends to reduce the electron-withdrawing effect of the carbon–hydrogen bond and make the methyl group less electronegative. Miller, *et al.*,[2] observed that the C–D bond length was 0.009 Å shorter and the D–C–D bond angle 12 min greater in the fully deuterated methyl group than in the ^{1}H species. The presence of this effect in other molecules was confirmed by Laurie and Hershbach.[1] The inductive effect involving a change in electronegativity of the methyl group is discussed by Halevi[5] and Van Hook.[12] Decreasing the electronegativity of the methyl group will increase the electronegativity difference across the C–Cl bond and therefore increase the ionic character of this bond. According to the Townes–Dailey theory,[10] the increase in ionic character will decrease the quadrupole coupling strength. Following this model our measurments indicate an increase in ionic character by 0.17% for the deuterated form. We should note that there will be further contributions to variation in quadrupole coupling on deuteration due to changes in hydrogen positions. The C–Cl bond length was observed to decrease by 0.0008 Å when the methyl group was fully deuterated.[13] This change in bond length may also be related to changes in electronegativity and this effect is in qualitative agreement with the above results from quadrupole coupling.

The quadrupole coupling strengths in methyl bromide are considerably larger so previous microwave results[14] may be analyzed to obtain quadrupole coupling variations with deuterium substitution for this molecule. In this case full deuteration of the methyl group leads to a decrease of 0.27% in quadrupole coupling. This is very similar to the decrease of 0.24% we observed in methyl chloride.

Our measurements of quadrupole coupling in CH$_3$^{35}Cl strength indicate a systematic decrease in electric field gradient at Cl on deuterium substitution. Further measurements on CH$_3$^{37}Cl show that the decreased field gradient is not a direct result of the increased mass of the methyl group. Therefore, it appears that the chemical properties of the methyl group are modified by deuterium substitution.

Acknowledgment. This research was supported by the National Science Foundation.[15] The authors would like to thank George Whitesides and Tom Cromartie for helpful comments on this paper.

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[12] W. A. Van Hook, "Isotope Effects in Chemical Reactions," N. S. Bowman and C. J. Collins, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, pp 58–63.

[13] R. H. Schwendeman and J. D. Kelly, *J. Chem. Phys.*, **42**, 1132 (1965).

[14] B. Stark, "Molecular Constants from Microwave Spectroscopy," Vol. 4, K. H. Hellwege, Ed., Springer-Verlag, New York, N. Y., 1967.

[15] NSF Grant No. GP-21110—Structural Chemistry.

Laser-Excited Fluorescence Emission from Cis and Trans Isomers of 2,3- and 2,4-Dimethylcyclobutanone. Ultra-Short-Lived Excited Molecules[1]

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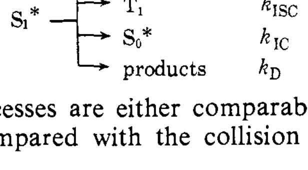
Contribution from the Department of Chemistry, University of California, Irvine, California 92664. *Received September 18, 1972*

Abstract: The singlet lifetimes (τ_s) of the dimethylcyclobutanone (DMCB) isomers are estimated by using the relationship $\tau_s = \tau_0 \Phi_F$ where τ_0 is the radiative lifetime and Φ_F is the measured quantum yield of fluorescence. τ_s for the DMCB isomers (S_1*) produced by uv-laser excitation at 325.0 nm is estimated as 0.3 nsec for *cis*-2,3-DMCB, 0.1 nsec for *trans*-2,3- and *cis*-2,4-DMCB, and 0.01 nsec for *trans*-2,4-DMCB. Facile α cleavage of the cyclobutanone ring "predissociation," facilitated effectively by α-methyl substitution, is held responsible for the observed short lifetimes in these "isolated" molecules in the gas phase, and some explanations are given for their variation. This α-substitution effect in the cyclobutanones is *opposite* to the α-substitution effect observed in the cyclopentanones and the cyclohexanones, since the singlet lifetimes of these C_5 and C_6 cyclic ketones are mainly determined by the $S_1 \rightsquigarrow T_1$ intersystem crossing rate ($\sim 10^9$ sec^{-1}). Practical limitation of measuring the weak luminescence signal and general validity of estimating the ultrafast transformation rates of the electronically excited molecules are briefly discussed.

Fluorescence emission, if measurable, provides valuable kinetic information about primary unimolecular processes which largely govern the fate of the photoexcited carbonyl compounds. The fluorescence emission process competes with singlet–triplet intersystem crossing, internal conversion, and chemical decomposition (and/or isomerization) on the first excited singlet manifold as shown in Scheme I. If these unimolecular processes are either comparable to or relatively slow compared with the collision frequency of

Scheme I



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[1] This research has been supported by National Science Foundation Grant GP-28010X.

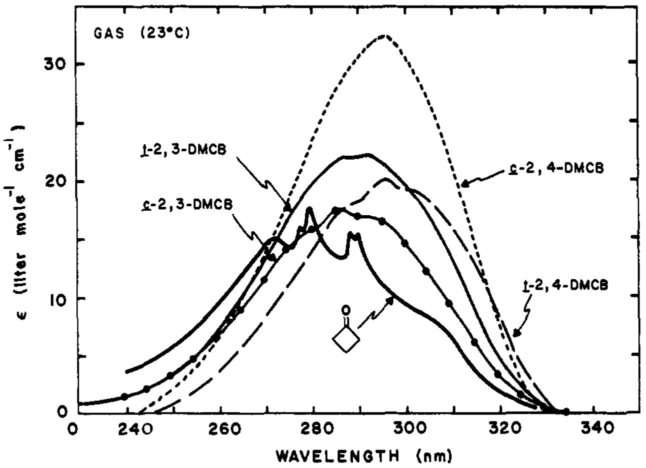
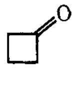
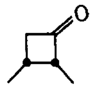


Figure 1. Molar extinction coefficients (M^{-1} cm^{-1}) for gaseous samples of cyclobutanone and four isomers of DMCB.

S_1* with other molecules in the system, the collisional processes would modify the intrinsic fate of S_1*.[2,3] The predominance of the nonradiative transitions (intramolecular and intermolecular) over the radiative transitions is so great in many systems of photochemical interest that the faint intensity of emission often limits the scope of investigation. We wish to report here the results of low-level fluorescence emission measurements achieved with a uv-laser excitation source which greatly exceeds the capability of the conventional luminescence spectrometers. Furthermore, we wish to illustrate the feasibility of estimating the rate of ultra-fast kinetic processes from the natural radiative lifetimes ($\tau_0 = 1/k_F$) and the measured fluorescence emission quantum yields (Φ_F) of cyclobutanone (CB) and cis and trans isomers of 2,3-dimethylcyclobutanone and 2,4-dimethylcyclobutanone (DMCB). Undoubtedly, the present study provides information important to the photochemistry of the DMCB isomers **2–5**.[4]


1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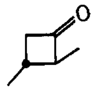
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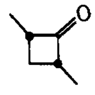
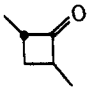

4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Experimental Section

The cyclobutanone used in this study was obtained from Aldrich Chemical Co. It was found to be of sufficient purity for use by gas chromatographic analysis. The DMCB isomers **2–5** were prepared and purified as described in a preceding paper.[4b] All samples were prepared on a grease- and mercury-free vacuum line.[4b]

The gas-phase absorption spectra were taken at room temperature on a Cary 14R spectrophotometer using a slidewire with the absorbance (*A*) range of 0.0–0.1 and a 50-mm path gas cell with Suprasil windows. The following pressures were used: **1** = 20 Torr; **2** = 11.5 Torr; **3** = 8.0 Torr; **4** = 6.0 Torr; **5** = 6.0 Torr. It was not convenient to measure photometrically the absorbance of the sample at the uv-laser wavelength (3250 Å, He-Cd laser, Spectra Physics Model 185, 15-mw, cw output) near the absorption threshold of the forbidden $\pi^* \leftarrow n$ transition of these ketones. Hence, we measured the relative absorptivity (ϵ_{rel}) indirectly by measuring the photolysis product yields (at low pressure of ketones **1–5**) from the laser irradiation. On the basis of the earlier photolysis studies,[2,4,5] we can safely assume that the photochemical decomposition product yields from these ketones are 1.0 at low pressures and λ_{ex} 325.0 nm. The photolysis products obtained at 0.50 Torr were analyzed by gas chromatography with a flame ionization detector.[4b] The observed yield data were appropriately corrected for the minor pressure quenching of the internal conversion products.[4]

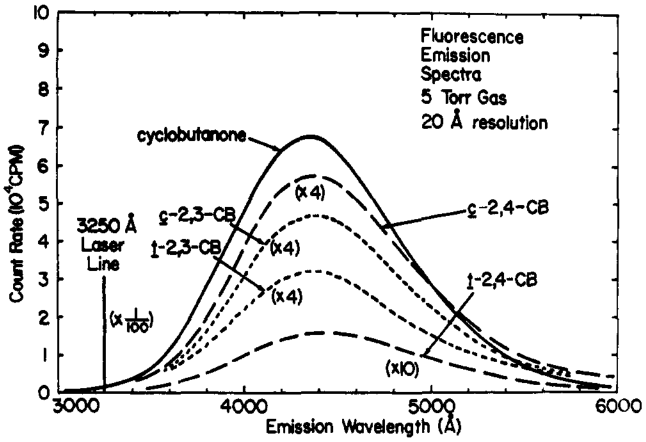

Figure 2. Laser-line (3250 Å) excited fluorescence emission spectra, uncorrected for the spectral sensitivities of detection components, of gaseous cyclobutanone (CB), *cis*- and *trans*-2,3-dimethylcyclobutanone (*c*- and *t*-2,3-DMCB), and *cis* and *trans*-2,4-dimethylcyclobutanone (*c*- and *t*-2,4-DMCB). Scale factors are indicated in parantheses.

A 1.3-mm diameter laser beam excited the gaseous ketone samples (5.0 Torr, 23°) contained in a T-shaped silica fluorescence cell equipped with 50-mm diameter flat-windows. A pair of silica lenses (51-mm diameter, *fl* = 75 and 100 mm) focused the fluorescent image onto the entrance slit of a 0.75-m monochromator (Spex Industries Model 1702, *f* = 7, 0.1 mm/Å dispersion, 5000-Å blaze). The emission spectra were obtained at 20-Å resolution. When the laser beam was condensed in order to collect more light into the narrow slit of the monochromator, a white spot of unknown composition which gave off-green emission built up on the cell window. It was found that the addition of 2 Torr of O_2 greatly slowed down the rate of deposition on the window. However, attempts to observe structured emission from cyclobutanone failed at 0.5-Å resolution.

The optical output from the exit slit was focused onto a cooled photomultiplier tube (−30°) with S-13 response (EMI 6252B). The output pulse from the PMT was fed into the photon counting system consisting of the following electronic modules in series: preamplifier/amplifier/integral discriminator (Harshaw Hamner Models NB-11/NA-11/NC-10); digital count rate meter/teletype scanner (Canberra Industries Model 6381/1488); teletype (Model 33). The photon counts accumulated for a time interval sufficient to give satisfactory counting statistics and signal/noise ratio were digitally recorded during the wavelength scan. A count rate of ≤1 pulse/sec was obtained as "dark" signal.

Attempts to measure the fluorescence decay time (τ_F) of the DMCB isomers as well as their fluorescence excitation spectra have so far failed when the apparatus used for cyclobutanone was employed.[3b,5d]

Results and Discussion

Absorption spectra of all five ketones **1–5** are shown in Figure 1, and their emission spectra (uncorrected for the spectral sensitivity of the setup) are shown in Figure 2. It is not too surprising to find that the emission profiles are all alike, since they involve $\pi^* \leftarrow n$ transitions with similar intensity distributions. A red shift of 7–8 nm per CH_3 substitution at α carbon is apparent in

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(2) R. B. Cundall and A. S. Davies, *Progr. React. Kinet.*, **4**, 147 (1967).

(3) (a) R. G. Shortridge, Jr., C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1863 (1971); (b) G. M. Breuer and E. K. C. Lee, *J. Phys. Chem.*, **75**, 989 (1971); we use here a revised value of $\tau_F = 4.9 \pm 0.2$ nsec for cyclobutanone (see ref 5d).

(4) (a) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 4482, 6683 (1970); (b) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *ibid.*, **94**, 7221 (1972).

(5) (a) T. H. McGee, *J. Phys. Chem.*, **72**, 1621 (1968); (b) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969); (c) J. C. Hemminger, C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1867 (1971); (d) J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, **56**, 5284 (1972).

Table I. Observed Absorption Coefficients (ϵ and ϵ_{rel}) and Fluorescence Quantum Yields (Φ_F)

Molecule	ϵ, M^{-1} cm^{-1} [a]	ϵ_{rel} (laser)[b]	I_F	Φ_F (laser)[c]
CB	0.7 ± 0.1	(1.00)	(1.00)	$(1.9 \pm 0.5) \times 10^{-3}$
cis-2,3-DMCB	1.6 ± 0.2	2.4 ± 0.2	0.14	$(11 \pm 2) \times 10^{-5}$
trans-2,3-DMCB	2.3 ± 0.3	3.2 ± 0.2	0.10	$(6 \pm 1) \times 10^{-5}$
cis-2,4-DMCB	3.1 ± 0.3	4.7 ± 0.3	0.17	$(7 \pm 1) \times 10^{-5}$
trans-2,4-DMCB	4.5 ± 0.4	7.2 ± 0.4	0.023	$(6 \pm 2) \times 10^{-6}$

[a] Values obtained with Cary 14 spectrophotometer runs. [b] Values obtained with the photodecomposition runs using a 3250-Å line of He–Cd laser. [c] The value for cyclobutanone was determined near 320 nm (ref 3a), and the values for the DMCB isomers (laser excitation at 3250 Å) are calibrated against the CB value. Only precision is indicated for the DMCB isomers.

Table II. Estimated Radiative Lifetimes (τ_0), Singlet Lifetimes (τ_s), and Quantum Yields of Intersystem Crossing (Φ_{ISC})

Molecule	$\tau_{0(S-B)}^{calcd}$, μsec[a]	τ_0, μsec[b]	τ_s, nsec[c]	Φ_{ISC}[d]
CB	9.0	(2.6)	(4.9 ± 0.2)	(1.0)
cis-2,3-DMCB	8.7	2.5	0.2_8	~0.04
trans-2,3-DMCB	7.6	2.2	0.1_3	~0.02
cis-2,4-DMCB	3.9	1.1	0.08	~0.01
trans-2,4-DMCB	8.3	2.4	0.01_4	~0.002

[a] Calculated from integrated absorption coefficients using eq 2 (ref 7). [b] The value of 2.6×10^{-6} sec for CB was measured near 320 nm as $\tau_0 = \tau_F/\Phi_F$ (ref 3b), and the values of τ_0 for the DMCB isomers were estimated as $\tau_0 = \tau_0^{calcd}(\tau_0/\tau^{calcd})_{CB}$. [c] The value of $\tau_F = (4.9 \pm 0.2) \times 10^{-9}$ sec for CB was measured near 320 nm (ref 3b), and the values of τ_s (λ_{ex} 325.0 nm) for the DMCB isomers were estimated as $\tau_s = \tau_0 \cdot \tau_F$. [d] The values of Φ_{ISC} for the DMCB isomers at λ_{ex} 3250 Å were estimated by $\Phi_{ISC} \approx k_{ISC} \cdot \tau_s$ as in eq 3.[13]

absorption. Due to the narrow line width of the laser radiation and the probable narrow absorption line width of the sample, the degree of the laser line absorption is more safely estimated by the use of ϵ_{rel} (photolytic) rather than by the spectrophotometric value of ϵ at low resolution. Hence, we use ϵ_{rel} for obtaining Φ_F,rel (= emission intensity/ϵ_{rel}),[6] recognizing the consistency of ϵ_{rel} with ϵ. The integrated emission intensities were measured relative to cyclobutanone, and the absolute values of Φ_F at λ_{ex} 325.0 nm for the DMCB isomers were evaluated on the basis of the known value of $\Phi_F = 0.0019$ at $\lambda_{ex} \approx 320$ nm for cyclobutanone.[3a] The results are summarized in Table I.

The value of the singlet state lifetime (τ_s) can be obtained from the following expression, where τ_0 is the radiative lifetime

$$\tau_s = \Phi_F \cdot \tau_0 \qquad (1)$$

if the experimental value of $\Phi_F = k_F/(k_F + k_{ISC} + k_{IC} + k_D)$ and the estimated value of τ_0 are known. The value of τ_0 can be calculated using the Strickler–Berg expression,[7] if the absorption and emission spectra are measured.

$$1/\tau_0^{calcd} = 2.880 \times 10^{-9} n^2 \langle \nu_f^{-3} \rangle_{av}^{-1} (g_l/g_u) \int \frac{\epsilon}{\nu}\, d\nu \qquad (2)$$

If the fluorescence decay time (τ_F) can be measured directly, the experimental and calculated values of τ_0 may be compared, since $\tau_0 = \tau_F/\Phi_F$ holds true also. For cyclobutanone, the experimental value of $\tau_0 = 4.9 \times 10^{-9}$ sec/0.0019 $= 2.6 \times 10^{-6}$ sec is a factor of 3.4 lower than the calculated value of $\tau_0^{calcd} = 9.0 \times 10^{-6}$ sec (see Table II). This degree of agreement is considered reasonable, since the S–B expression does not guarantee an accurate estimate for forbidden transitions of weak intensity and also for transitions with lack of the "mirror symmetry" which is due to a large change in the equilibrium geometries between the excited and the ground states. But it should be noted that for benzene and its methylated derivatives where the weak transition of the type ($^1B_{2u}$–$^1A_{1g}$) is only vibronically allowed and the geometry change is relatively small,[8a] τ_0^{calcd} obtained from the S–B expression agrees well with the experimental τ_0 value (gas phase).[8b,c]

A quantitative treatment of the geometry change correction factor has been carried out recently for the H_2CO ($^1A_2 \leftrightarrow {}^1A_1$) system by Barnhart and Strickler,[9] and the corrected value of τ_0 is 3–4 times shorter than that calculated from the S–B expression. We find that experimentally obtained values of τ_0 for the radiative transitions of a few ketones[3b] ($\pi^* \leftrightarrow$ n or $^1A_2 \leftrightarrow {}^1A_1$) are ~0.2 times the values of τ_0^{calcd} (S–B): τ_0/τ_0^{calcd} is 1.8 μsec/9.6 μsec $\approx$ 0.19 for cyclohexanone; 1.7/9 $\approx$ 0.19 for cyclopentanone; and 1.3/8.7 = 0.15 for acetone. Our last value is comparable to the value of 2.0/10 = 0.20 obtained by Halpern and Ware.[10] It is well known that the $^1A_2$ states of H_2CO,[11] cyclobutanone,[12a,b] and cyclopentanone[12c] are nonplanar (near the chromophore) unlike the planar ground state, and the C=O bond has an out-of-plane carbonyl angle of 20–31° and has stretched out ~0.10 Å. In view of these facts we could rationalize the discrepancy between the observed value of τ_0 and the calculated value of τ_0^{calcd} (S–B). A quantitative calculation of the geometry change correction factor for cyclobutanones would require a great deal of spectroscopic data and analysis which is unavailable at present. Since consistently larger estimates of τ_0^{calcd} (S–B), a factor of 3–6, result from the use of the S–B expression for several simple ketones,[3b] it can be justified to normalize the calculated values of τ_0^{calcd} for the DMCB isomers to the experimental value of τ_0 obtained for cyclobutanone. The values of τ_S (325.0 nm) for the DMCB isomers are

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(6) Within the accuracy of measurement, the values of ϵ_{rel} compare reasonably to the values of ϵ obtained spectrophotometrically.

(7) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962). We used $n = 1.00$, $g_u = g_l = 1$, and $\langle \nu_f^{-3} \rangle_{av}^{-1} = 1.3 \times 10^{13}$ (cm^{-1})^3 for the singlet $\pi^* \leftarrow$ n transition for the five ketones.

(8) (a) J. H. Callomon, T. M. Dunn, and I. M. Mills, *Phil. Trans. Roy. Soc. London, Ser. A*, **259**, 449 (1966); (b) G. M. Breuer and E. K. C. Lee, *Chem. Phys. Lett.*, **14**, 404 (1972); (c) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(9) R. J. Bahnhart and S. J. Strickler, University of Colorado, private communication of their unpublished results.

(10) A. M. Halpern and W. R. Ware, *J. Chem. Phys.*, **54**, 1271 (1971).

(11) V. A. Job, V. Sethuraman, and K. K. Innes, *J. Mol. Spectrosc.*, 30, 365 (1969), and references cited therein.

(12) (a) D. C. Moule, *Can. J. Phys.*, **47**, 1235 (1969); (b) W. D. Chandler and L. Goodman, *J. Mol. Spectrosc.*, **35**, 232 (1970); (c) H. E. Howard-Lock and G. W. King, *ibid.*, **36**, 53 (1970).

then calculated from eq 1 using these normalized values of τ_0, as shown in Table II. The τ_s values thus calculated are probably accurate to within a factor of $\sim$3 but they are likely to be very consistent among the isomers.

Obviously, the S_1 state of all four DMCB isomers predissociates at λ_{ex} 325.0 nm,[5c,d] consistent with the photochemical observation. The fact that the 2,3-DMCB (S_1*) is one to two orders of magnitude and the 2,4-DMCB (S_1*) is two to three orders of magnitude shorter lived than CB (S_1*) indicates strongly that the *CH_3 group substituted at α carbon drastically aids the rate of cleavage of the C_1–C_2 (C_1–C_4) bond* and ring-opened biradicals are efficiently generated.[4] If it is true that the energy level of the first excited singlet state of the 2,4-DMCB (S_1) is somewhat lower (1–2 kcal/mol) than that of the 2,3-DMCB (S_1), then the S_1 state produced at λ_{ex} 325.0 nm from the 2,4 isomer could have more vibrational excitation energy than that from the 2,3 isomers. k_{ISC} for CB is estimated[3b,5d] to be 2×10^8 sec^{-1}, and it is reasonable to estimate somewhat lower values for the DMCB isomers.[3b,13,14] It is also reasonable now to neglect the *direct* internal conversion process (k_{IC}) on the basis of the detailed photodecomposition study.[4] Thus, the ring-opening process (k_D) will clearly predominate over the $S_1 \rightsquigarrow T_1$ intersystem crossing process (k_{ISC}) in deactivating the DMCB (S_1*) at λ_{ex} 325.0 nm. It can be shown that

$$\Phi_{ISC} = k_{ISC} \cdot \tau_s \qquad (3)$$

The relative values of Φ_{ISC} thus estimated[13] are shown in Table II, and they are definitely compatible with the photochemical decomposition results.[4b,15]

It is interesting to note the strikingly reverse trend in the unimolecular decomposition rates among the S_1* species and the S_0* species: k_D values for S_1* are in order of *trans*-2,4-DMCB > *cis*-2,4-DMCB > *trans*-2,3-DMCB > *cis*-2,3-DMCB whereas k(E) values at λ_{ex} 325.0 nm for S_0* are in order of *cis*-2,3-DMCB > *trans*-2,3-DMCB > *cis*-2,4-DMCB ≈ *trans*-2,4-DMCB.[16] A clear difference in the reactivities of S_1* and S_0* is well manifested. It would be very interesting to correlate quantitatively, through future studies, the predissociation rates with the size and shape of the energy barrier and the excess vibrational energy content. It is known that the singlet (n,π*) excited state of cyclobutanone has an appreciable inversion barrier for the out-of-plane wagging mode of the O atom.[12] Therefore, the excited DMCB (S_1*) can have two possible conformations for the α-CH_3 group, either cis or trans with respect to the carbonyl O atom. Though details are not known, it is conceivable that the greatly reduced value of τ_s ($^1/_6$) for *trans*-2,4-DMCB (S_1*), compared to τ_s for *cis*-2,4-DMCB (S_1*) having no more than 5 kcal/mol vibrational excitation energy,[12a] may be the result of their conformational stabilities; *trans*-2,4-DMCB has one conformation, cis–trans for the two α-CH_3 groups, whereas *cis*-2,4-DMCB has two possible conformations, trans–trans and cis–cis. It is a fact that in the ground state *cis*-2,4-DMCB is more stable than *trans*-2,4-DMCB due to the preference of the α-CH_3 groups to be *equatorial*.[17] It is probably so in the excited state. It could be that ring puckering and the O-atom wagging mode (out-of-plane) lead to significant O-atom/axial CH_3-group interactions, and hence a shorter singlet lifetime of trans-2,4 isomer results. Such interactions need not be present for the cis-2,4 isomer in which the CH_3 groups could be both equatorial. Further studies should bring out the necessary experimental evidence for the role the conformational stabilities play in the excited state kinetics.

The utility of the weak fluorescence emission measurement in estimating the ultra-short lifetimes of the excited singlet species is well demonstrated above. The laser excitation coupled with a photon counting method increases the sensitivity greatly. The validity of using eq 1 and 2 is well established here and elsewhere.[3,18] We estimate that we could readily measure a value of Φ_F yet lower by three orders of magnitude, 1×10^{-8}, and a corresponding τ_s yet shorter by three orders of magnitude, 1×10^{-14} sec,[19] for more optically dense samples, because the present gaseous sample had absorbed only 0.1% of the laser radiation per 10-mm path. Other improvements in the luminescence collection would undoubtedly lower the practical limit of Φ_F (or Φ_P) determination and shorten the time scale of measurement, as the choice of an excited molecular species having an intrinsically shorter value of τ_0 would also shorten the temporal limit. High-resolution studies should be possible, when the window-fogging problem accompanying the condensed laser beam is solved.

Acknowledgment. We are grateful to Professor S. J. Strickler for timely helpful discussion of their calculation on the geometry correction factor in formaldehyde and for permitting us to use their preliminary result.

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(13) The singlet lifetimes near the absorption threshold of the α-CH_3-substituted cyclic (C_5; C_6) and aliphatic ketones are *consistently longer* compared to those of the unsubstituted ketones. This reflects slower rates of $S_1 \rightsquigarrow T_1$ intersystem crossing in these substituted ketones (see ref 3b and 14). We will assume that k_{ISC} for the 2,3-DMCB isomers is 1.5×10^8 sec^{-1} and k_{ISC} for the 2,4-DMCB isomers is 1.0×10^8 sec^{-1}.

(14) (a) J. C. Dalton, D. M. Pond, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2173 (1970); (b) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 6974 (1970).

(15) The yield of dimethylcyclopropanes as well as the trans/cis ratio in dimethylcyclopropanes reflects the triplet yield in the DMCB photodecomposition.[4] The fact that trans/cis ratios obtained with *cis*-2,3-DMCB increase (reversing the trend in stereoretention) from a value of 0.7 at λ_{ex} 313 nm to 1.0 at 325.0 nm and 1.3 at 334 nm indicates that a few per cent at 325.0 nm and over 10% of *cis*-2,3-DMCB (S_1*) at 334 nm intersystem cross (see Figure 3 in ref 4b); also, consistently higher values of the dimethylcyclopropanes yield are observed than expected by extrapolation of the values obtained in the "pure" singlet domain ($\lambda_{ex} \leq 313$ nm) for *cis*-2,3-DMCB (see Table XII in ref 4b). A similar trend but of lesser degree is also observed in the photolysis of *trans*-2,3-DMCB as expected.

(16) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **94**, 7235 (1972).

(17) N. J. Turro and R. B. Gagosian, *ibid.*, **92**, 2036 (1970). An equilibrium study indicates that **3** is more stable than **2** (by $\Delta F = -0.71$ kcal/mol) and **5** is less stable than **4** (by $\Delta F = +0.52$ kcal/mol).

(18) See, for example, J. C. Dalton and N. J. Turro, *ibid.*, **93**, 3569 (1971), for the application made in solution.

(19) The expected line width for such a short-lived species is 5×10^2 cm^{-1}.