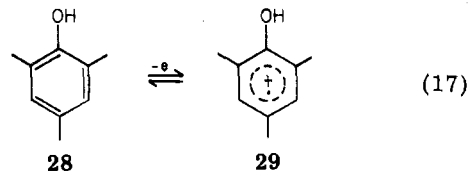**Figure 7.** Approximate pH–potential diagram for a 2,4,6-tri-alkylphenol in acetonitrile. Line segment bc is at the level of the phenol/phenol cation radical couple (POH/POH^{+}·);[38] line de is at the phenoxy radical/phenoxonium ion potential (PO·/PO^{+});[3] line fg is the phenoxide/phenoxy couple (PO^{-}/PO·);[3] and fh is at the pK_a of the phenol in acetonitrile.[48] Line cd represents the pH dependence of the potential of the PO^{+} + H^{+} + 2e = POH couple; line df is for the PO· + H^{+} + e = POH couple. Abscissa is a combined pH/acidity function scale.

Two schemes seem most probable. The first is a type of ECE process which involves initial formation of radical cation (DPA^{+}·) followed by addition of pyridine, oxidation, and, finally, addition of a second pyridine, giving DPA·Py$_2$$^{2+}$.[41]

The second scheme involves disproportionation of the radical cations giving the dication which is rapidly pyridinated. These two schemes have proven to be quite difficult to distinguish by voltammetry, but more definitive results have been obtained by supplementary application of other techniques. For example, the rate of disappearance of DPA^{+}· has been measured by visible absorption spectroscopy following electrochemical generation of the radical cation at a transparent electrode.[42] The pyridination reaction was shown to

(41) G. Manning, V. D. Parker, and R. N. Adams, *J. Am. Chem. Soc.*, **91**, 4584 (1969).

$$(17)$$

28   **29**

proceed via the ECE scheme. A simple and direct procedure was employed by Svanholm and Parker[43] who generated known concentrations of DPA^{+}· in superdry media using an anode of large surface area and known constant currents. They then used a rotating disk electrode to monitor the concentration of DPA^{+}· as it reacted with pyridine in homogeneous solution. Their results strongly support the ECE scheme. This technique has been applied to other anodic reactions in which even more complex rate laws have been found.[44-46] Similar ECE schemes are operative in the reduction of quinones in the presence of proton donors.[47]

The foregoing journey through recent work in electrochemistry shows that many electrode reactions fall in the class of weakly interacting systems in which the electrochemically generated intermediates diffuse into solution where they display their inherent chemical properties. Voltammetry provides thermodynamic and kinetic information concerning the species participating in the reaction, and in this way gives new insight into chemical properties.

(42) H. N. Blount, *J. Electroanal. Chem.*, **42**, 271 (1973).

(43) U. Svanholm and V. D. Parker, *Acta Chem. Scand.*, **27**, 1454 (1973).

(44) U. Svanholm, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 101 (1975).

(45) U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **98**, 997 (1976).

(46) U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **98**, 2942 (1976).

(47) R. M. Wightman, J. R. Cockrell, R. W. Murray, J. N. Burnett, and S. B. Jones, *J. Am. Chem. Soc.*, **98**, 2562 (1976).

(48) J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **69**, 3193 (1965).

Laser Photochemistry of Selected Vibronic and Rotational States

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Many of the photochemical studies in the last several decades have dealt with the elucidation of the mechanisms which give satisfactory quantitative account of the observed final photoproducts, and some have been very successful in providing the detailed information

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about the roles each excited electronic state plays in various primary photochemical processes.[1] While the reactivity of the excited states is of general interest, the physical properties of the excited states which give rise to instability as manifested by luminescence, radiationless transition, predissociation, dissociation, molecular rearrangement, etc., are of more fundamental interest. However, less is known about these

(1) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966; (b) N. J. Turro, "Molecular Photochemistry", Benjamin, New York, N.Y., 1965; (c) J. P. Simons, "Photochemistry and Spectroscopy", Wiley-Interscience, New York, N.Y., 1971.

"nonstationary" state properties than the "stationary" state properties of the excited states such as energy, angular momentum (electronic spin and orbital), geometry, etc. For the latter, fairly advanced knowledge has been developed through spectroscopic and theoretical studies. In particular, the radiationless processes play an important role in primary photochemical transformations, and the early theoretical treatments[2] have initiated an avalanche of recent experimental and theoretical studies.[3]

Since photochemical reactions depend on the existence of and the nature of radiationless processes and often a variety of vibronic coupling mechanisms plays a key role in radiationless transitions,[3] a significant amount of recent research effort has been devoted to the radiationless transitions in "small" polyatomic molecules in which the behavior of single vibronic levels (SVL) can be followed through resonance fluorescence emission spectroscopy,[3e,4] fluorescence excitation spectroscopy,[5] lifetime measurement,[6] and dissociation product measurement.[5a,6c,7] Since the advent of tunable dye lasers, one no longer needs to encounter the earlier experimental difficulty of achieving monochromatic photoexcitation to a set of desired single vibronic levels using the conventional combination of a continuum arc lamp and a moderate resolution monochromator.[4-7] Dye lasers have even made possible the study of the selected rotational states in small polyatomic molecules at low pressures and have provided some crucial and fascinating insight into various mechanisms of the radiationless transitions. I wish to describe briefly some of the recent progress made by my research group in this direction.

Reactivity of Electronically Excited States.

It was mentioned earlier that what makes photochemistry interesting in general is the distinct variation of reactivity among different electronic states. The most popular theoretical justification for this has been presented through the principle of the conservation of orbital symmetry,[8] and there is no need to elaborate on it here. But, if the supposition that the final products given by the ground electronic state of a molecule differ distinctly from those given by the lower excited electronic states is true, this system has the most important
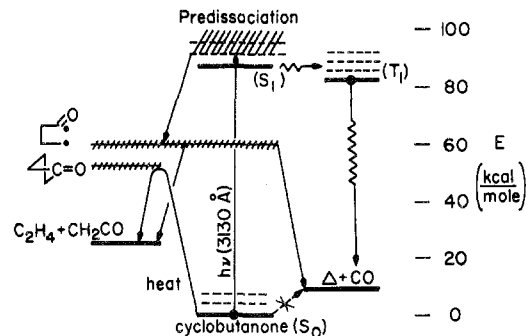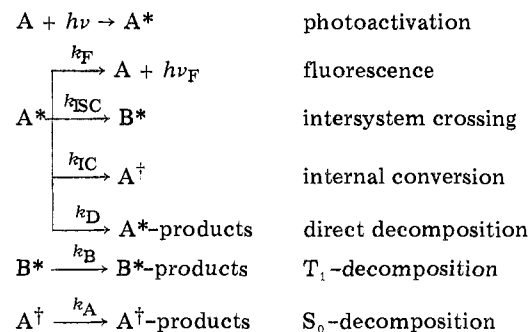
(2) (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963); (b) G. R. Hunt, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, **15**, 591 (1962).

(3) (a) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, **7**, 149 (1969); (b) B. R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.*, **18**, 161 (1968); (c) E. W. Schlag, S. Schneider, and S. F. Fischer, *ibid.*, **22**, 465 (1971); (d) B. R. Henry and W. Siebrand, "Organic Molecular Photophysics", Vol. 1, J. B. Birks, Ed., Wiley, New York, N.Y., 1973, p 153; (e) C. S. Parmenter, *Adv. Chem. Phys.*, **22**, 365 (1972).
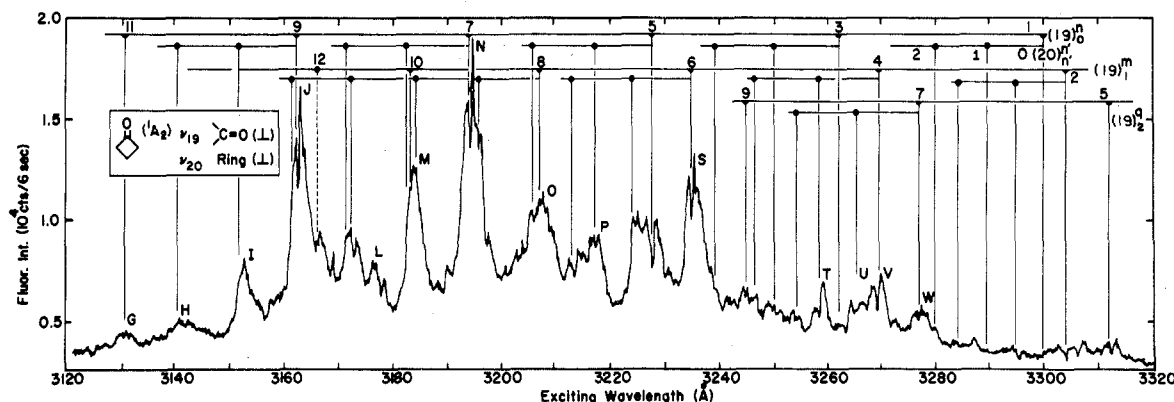
(4) (a) C. S. Parmenter and M. W. Schuyler, *Transitions Non Radiat. Mol., Reun. Soc. Chim. Phys., 20th, 1969*, 92 (1970); (b) H. F. Kemper and M. Stockburger, *J. Chem. Phys.*, **53**, 268 (1970); (c) see C. S. Parmenter, *MTP Int. Rev. Sci., Phys. Chem., Ser. One*, **3**, 297 (1972).

(5) (a) J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, **56**, 5284 (1972); (b) R. G. Miller and E. K. C. Lee, *Chem. Phys. Lett.*, **33**, 104 (1975).

(6) (a) B. K. Selinger and W. R. Ware, *J. Chem. Phys.*, **53**, 3160 (1970); (b) K. G. Spears and S. A. Rice, *ibid.*, **55**, 5561 (1971); (c) A. S. Abramson, K. G. Spears, and S. A. Rice, *ibid.*, **56**, 2291 (1972); (d) E. S. Yeung and C. B. Moore, *ibid.*, **58**, 3988 (1973); (e) R. A. Beyer, P. F. Zittel, and W. C. Lineberger, *ibid.*, **62**, 4016 (1975).

(7) (a) R. S. Lewis, K. Y. Tang, and E. K. C. Lee, *J. Chem. Phys.*, **65**, 2910 (1976); (b) W. M. Uselman and E. K. C. Lee, *ibid.*, **65**, 1948 (1976); (c) K. Y. Tang and E. K. C. Lee, *J. Phys. Chem.*, **80**, 1833 (1976).

(8) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1969; (b) L. Salem, *Science*, **191**, 822 (1976).

Figure 1. Reaction pathways of cyclobutanone from its S_1, T_1, and S_0 states.

qualification as a model worthy of study. The competition between two channels of radiationless processes as well as the dynamics of photodissociation can be studied as a function of excitation energy, the symmetry of the vibronic state, the mode of the vibration excited, etc. Among other qualifications required for the model are, for example, the possibility of achieving a selective excitation of the SVL's by virtue of the absence of vibronic band overlap in the absorption spectrum, the availability or the feasibility of the reliable vibrational state assignment, and the presence of molecular luminescence in the gas phase.

Cyclobutanone was chosen for the initial study of single vibronic level photochemistry. Since the electric dipole forbidden, vibronically allowed $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ transition to the $n\pi^*$ state of cyclobutanone was found to be highly structured, the vibrational assignments of the observed absorption bands were given by Moule,[9] and the molecular fluorescence can be observed,[10c] the above spectroscopic criteria were adequately met. In the earlier studies[10] it was established that: (1) the triplet state (T_1) of cyclobutanone (CB) decomposes to cyclopropane and carbon monoxide by photodecarbonylation, (2) at low photoexcitation energy the singlet state (S_1) primarily undergoes S_1 to T_1 intersystem crossing, (3) at high photoexcitation energy the singlet state undergoes S_1 to S_0 internal conversion, (4) the resulting hot ground state $(S_0^\dagger)$ decomposes unimolecularly to ethylene and ketene by concerted cycloreversion process, and (5) the molecular predissociation

(9) (a) D. C. Moule, *Can. J. Phys.*, **47**, 1235 (1969); (b) a more recent report gives the revised assignment of the vibronic transitions involving the out-of-plane ring puckering (ν'_{20}) in the upper state, as the sequence band rather than the progression: D. C. Moule, *J. Chem. Phys.*, **64**, 3161 (1976).

(10) (a) H. O. Denschlag and E. K. C. Lee, *J. Am. Chem. Soc.*, **90**, 3628 (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. Am. Chem. Soc.*, **93**, 1867 (1971).

Figure 2. Fluorescence excitation spectrum of cyclobutanone at 30 torr and 0.2-Å spectral resolution. The total intensity of fluorescence emission was recorded as a function of the exciting wavelength. For example, $19_1{}^3$ denotes a hot-band transition $\nu'_{19} = 3 \leftarrow \nu''_{19} = 1$.

sets on with the excitation by Hg 3130-Å line. This is schematically shown in Figure 1. There the radiationless processes of items 2 and 3 are designated as $S_1 \rightsquigarrow T_1$ and $S_1 \rightsquigarrow S_0$, respectively, where a wavy arrow denotes the radiationless process, as distinct from a straight arrow for the radiative transitions. Furthermore, a deeper insight into the photochemical transformation mechanism was provided from the stereochemical studies of the dimethyl-substituted cyclobutanones.[11] Therefore these experimental data were supportive of the feasibility of the SVL photochemical study of cyclobutanone.

Wavelength Dependence and Vibronic State Selection

The set of primary processes shown in Scheme I under "isolated molecule" conditions should be considered for a molecule after an SVL excitation. If the direct decomposition channel can be ignored, we have only three competing relaxation channels to consider, and the efficiency of each process can be measured as quantum yields of fluorescence, "triplet" product and "hot ground state" products. The competition between the two nonradiative channels can be then determined from the product ratio. The fluorescence quantum yield (Φ_F) for each SVL can be obtained conveniently from the comparison of the absorption and the fluorescence excitation spectra (eq 1), where I_F is the fluorescence

$$\Phi_F = \frac{I_F}{I_a} \tag{1}$$

intensity and I_a is the absorbed intensity of a given vibronic transition. The measurement of the fluorescence decay time, τ_F, is needed for the determination of the radiative (fluorescence) rate, k_R (eq 2), and the

$$k_R = \Phi_F/\tau_F \tag{2}$$

total nonradiative rate, k_{NR} (eq 3), which is equal to the

$$k_{NR} = (1 - \Phi_F)/\tau_F \tag{3}$$

sum of k_{ISC}, k_{IC}, and k_D. The observed product ratio (from B* and A†) gives the branching ratio of k_{ISC} and k_{IC}.

The fluorescence excitation spectrum of cyclobutanone is shown in Figure 2, and it illustrates the onset of the molecular predissociation and the pertinent

vibronic structure.[5a] Since the absorption spectrum for the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ transition extends from 3400 to 2400 Å with its absorption maximum at ~2800 Å, this figure clearly indicates that the fluorescence emission yield dies out suddenly near 3200 Å, where the value of Φ_F is ~0.002.[10c,12] This behavior is unique for cyclobutanone and some of its derivatives and is not observed in noncyclic and other larger cyclic ketones.
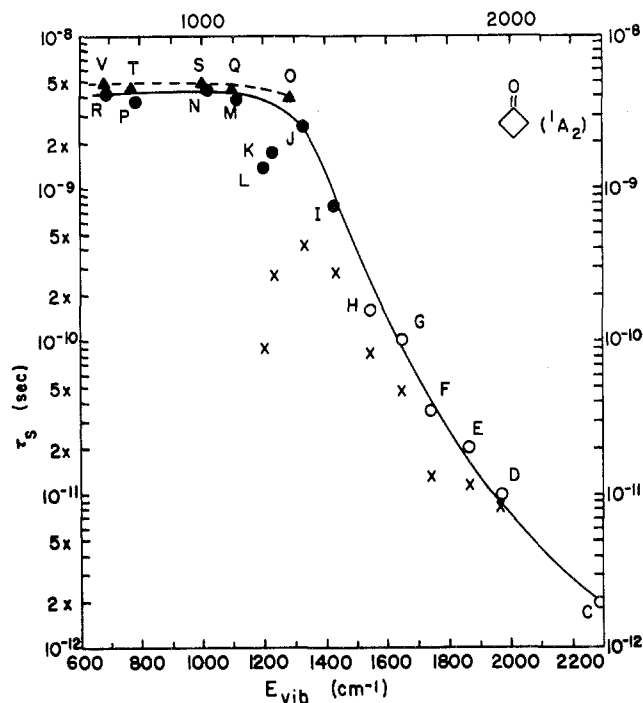
Two upper state vibrations which are active in the $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ transition are:[9] $\nu'_{19} = 335$ cm^{-1}, the out-of-plane wagging of O atom, and $\nu'_{20} = 134$ cm^{-1}, the out-of-plane ring puckering. The progression built on ν'_{19} with an odd quantum number change in ν_{19} becomes intense at a high value of the quantum number, because the equilibrium geometry of the excited state is nonplanar about the carbonyl C atom, and this results in an inversion doubling potential. The hot band transitions $(19)_1{}^m$ and $(19)_2{}^q$ are quite strong above 3200 Å.* The sequence band, e.g., $(20)_n{}^n$, built on ν'_{20} is somewhat weaker. In this notation, the number in parentheses refers to the vibration involved in the vibronic transition, e.g., ν_{19}. The superscript is the vibrational quantum number for the upper electronic state and the subscript is the vibrational quantum number for the lower electronic state.

The values of the SVL lifetime (τ_s) of the S_1 state which are approximately proportional to the SVL values of Φ_F are shown as a function of the vibrational energy of S_1 in Figure 3. If, instead, the lifetime values were plotted against the excitation wavelength, the smooth correlation observed in Figure 3 is no longer obtained, which indicates the obvious complexity of the wavelength dependence in the CB(S_1) relaxation process. For a comparison, Figure 4 shows the vibrational energy dependence of the product ratio of c-C_3H_6/C_2H_4, i.e., Φ_{ISC}/Φ_{IC}, from the recent laser photolysis study[7c] where the weaker absorbing peaks were excited and the monochromaticity is improved over the earlier study.[5a] The lifetime variation and the product ratio variation are consistent, showing that the onset of the molecular predissociation is due to the enhancement of the $S_1 \rightsquigarrow S_0$ internal conversion rate (k_{IC}). The onset energy is better determined to be $E_{vib} \simeq 700$ cm^{-1} in the laser experiment.[7c]
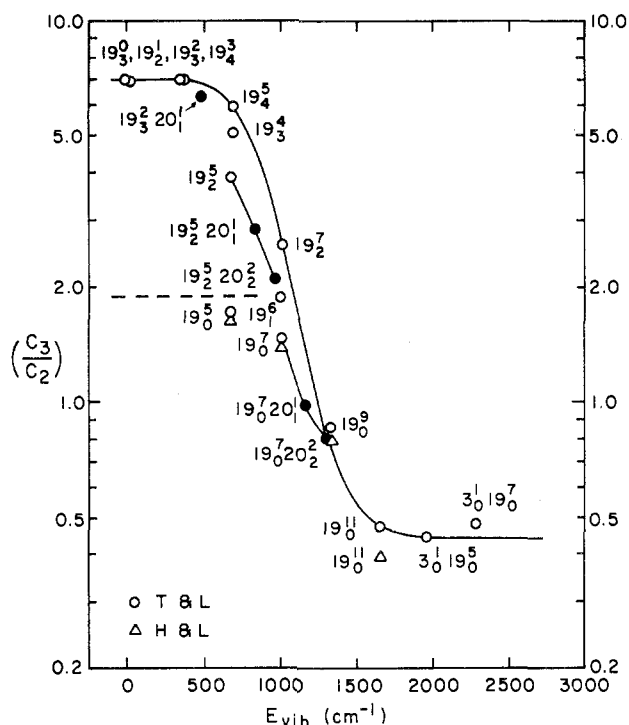
The results shown in Figure 4 provide information about the vibronic symmetry effect on the radiationless

(11) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *J. Am. Chem. Soc.*, **94**, 7221 (1972).

(12) J. C. Hemminger, H. A. J. Carless, and E. K. C. Lee, *J. Am. Chem. Soc.*, **95**, 682 (1973).

Figure 3. SVL decay time of CB(S$_1$) vs. vibrational energy (E_{vib}) of CB(S$_1$): directly measured cold band (●); directly measured hot band (▲); estimated cold band (○). Reprinted with permission from ref 5a. Copyright 1972 by the American Institute of Physics.

Figure 4. C$_3$/C$_2$ product ratio vs. E_{vib} of CB(S$_1$) where C$_3$ = cyclopropane and C$_2$ = ethylene. The recent laser experiment (circles) extended beyond the limit of the previous experiment (triangle) indicated by the broken line. (Figure 1 of ref 7c).

transition. For example, the vibronic symmetry of 19^4 and 19^6 is A$_1$, while that of the corresponding degenerate inversion doublets, 19^5 and 19^7, is B$_1$ if the symmetry of the "hidden" vibration is a$_2$.[9b] The C$_3$/C$_2$ ratio obtained from the 19$_4^5$ transition is greater than the ratio from the 19$_3^4$, and similarly the C$_3$/C$_2$ ratio obtained from the 19$_2^7$ transition is greater than the ratio from the 19$_1^6$ transition. Although the observed

differences are not large, the S$_1$ $\rightsquigarrow$ S$_0$ process is slightly more enhanced for the totally symmetric vibronic level (A$_1$) than for the degenerate level of the B$_1$ symmetry. This could be due to the effectiveness of the high frequency normal modes of totally symmetric vibronic species in CB(S$_0$) as the accepting modes.

The vibrational selectivity in the photodecomposition of NO$_2$(2^{2}B$_2$) to O(^{1}D) and NO(^{2}II) has also been studied,[7b] but it will not be discussed here.

The wavelength dependence of the formaldehyde photodecomposition was carefully studied by McQuigg and Calvert,[13] but the SVL photochemistry of H$_2$CO, HDCO, and D$_2$CO was first studied by Yeung and Moore.[6d] Undoubtedly, formaldehyde is ideally suited for an SVL study: There are only six vibrations, the spectroscopy of its $\tilde{A}^1A_2$-$\tilde{X}^1A_1$ system has been blessed with a number of definitive and detailed studies,[14] the vibrational structure of the electronic spectrum is well resolved as shown in Figure 5, two photodecomposition channels (radical pathway to give H + HCO and molecular pathway to give H$_2$ and CO) are present, and the isotopically labeled species provide additional handles. It is no accident that the well-known photochemical laser isotope separation experiment of Yeung and Moore was first carried out with formaldehyde. The illustration of the richness of the SVL photochemistry shall be illustrated below.

The fluorescence excitation spectrum of H$_2$CO obtained by Miller is shown in Figure 6,[15] and the values of τ_F and τ_R determined from the observed values of Φ_F and τ_F[5b] are shown in Figure 7. The first surprise is the enormous variation of τ_R with E_{vib} and the second surprise is the relatively slow onset of molecular predissociation unlike the case of cyclobutanone. So far no theory[16] of radiative transitions has given a satisfactory quantitative agreement with the experiment,[5b] but the slow exponential decrease of τ_{NR}, which nearly equals τ_F for H$_2$CO, has been qualitatively accounted for using the S$_1$ $\rightsquigarrow$ S$_0$ process as the dissipative mechanism.[17] Since more discussion of the mechanism of radiationless transitions will be given later, we shall turn to the product study.

The energy dependence and the vibronic state dependence of the two decomposition channels (eq 4) are

$$H_2CO + h\nu \begin{cases} \longrightarrow H + HCO & (4a) \\ \longrightarrow H_2 + CO & (4b) \end{cases}$$
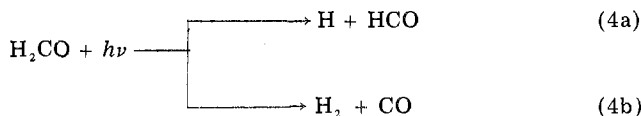
not only of theoretical interest from the point of view of chemical dynamics[18] but are also of practical interest to atmospheric chemistry[19] and laser isotope separation.[6d,20] The key question is what is the threshold

(13) R. D. McQuigg and J. G. Calvert, *J. Am. Chem. Soc.*, 91, 1590 (1969).
(14) (a) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956); (b) J. H. Callomon and K. K. Innes, *J. Mol. Spectrosc.*, 10, 166 (1963); (c) J. E. Parkin, *ibid.*, 15, 483 (1965); (d) V. A. Job, V. Sethuraman, and K. K. Innes, *ibid.*, 30, 365 (1969); (e) V. Sethuraman, V. A. Job, and K. K. Innes, *ibid.*, 33, 189 (1970).
(15) R. G. Miller, Ph.D. Thesis, University of California, Irvine, 1975.
(16) (a) E. S. Yeung, *J. Mol. Spectrosc.*, 45, 142 (1973); (b) G. R. Fleming, O. L. J. Gijzeman, and S. H. Lin, *Chem. Phys. Lett.*, 21, 527 (1973); (c) G. Orlandi and W. Siebrand, *J. Chem. Phys.*, 55, 4513 (1973).
(17) E. S. Yeung and C. B. Moore, *J. Chem. Phys.*, 60, 2139 (1974).
(18) R. L. Jaffe and K. Morokuma, *J. Chem. Phys.*, 64, 4881 (1976).
(19) (a) J. G. Calvert, J. A. Kerr, K. L. Demerjian, and R. D. McQuigg, *Science*, 175, 751 (1972); (b) M. Nicolet, *Rev. Geophys. Space Sci.*, 13, 593 (1975).
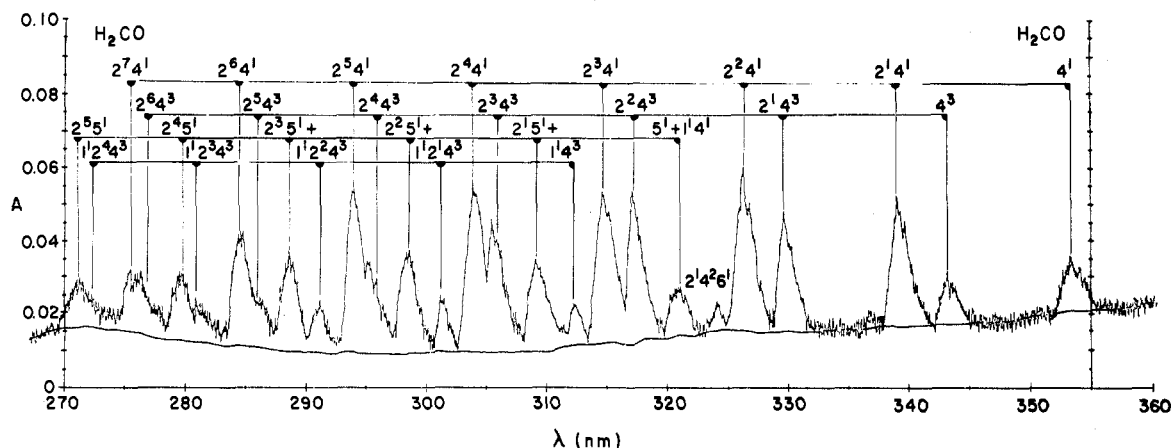
Figure 5. Absorption spectrum of H_2CO in the gas phase. The subscript for the Brand notation was omitted since all of the transitions shown are cold bands. ν'_2 = C–O stretch, ν'_4 = out-of-plane bending, and ν'_5 = antisymmetric C–H stretch.
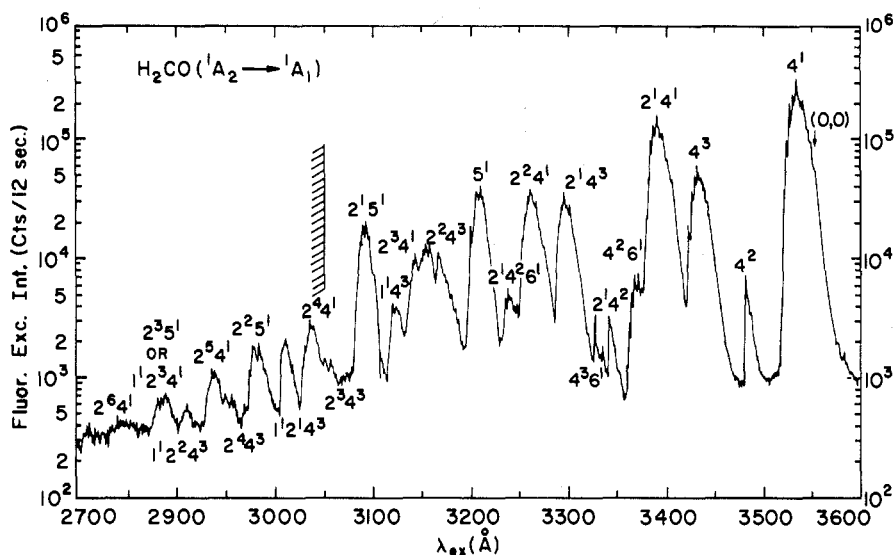
Figure 6. Fluorescence excitation spectrum of H_2CO at 1.0 torr. The subscript for the Brand notation was omitted since all of the transitions shown are cold bands. Reprinted with permission from ref 5b. Copyright 1975 by *Chemical Physics Letters*.

energy for the radical decomposition process.[4a] Our recent measurement of the wavelength dependence of the radical quantum yield indicates the threshold at ∼3300 Å, in agreement with the value recently obtained by Marling,[21] and the results are shown in Figure 8.[7a] Since the isotope selective photoexcitation becomes scrambled by the radical process, the isotope separation should be done at excitation wavelength longer than 3300 Å. In the above measurement,[7a] we have monitored the photochemical H-atom yield by detecting the red chemiluminescence at 762 nm from the electronically excited HNO ($\tilde{A}^1A''$) formed by the recombination of a hydrogen atom and NO in the H_2CO/NO mixture. The photoexcited chemiluminescence excitation spectrum corresponding to an "action" spectrum of the photochemical formation of a hydrogen atom is shown in Figure 9. This convenient spectroscopic detection technique has become indispensable for rotational state selection study since, as will be discussed later, the H-atom quantum yields from hundreds of individual

rotational levels can easily be recorded in a few hours of experiment. It appears from the results shown in Figure 8 that the values of Φ_H for the 2^34^3, 2^54^1, and 2^64^1 levels are lower than those for other SVL levels nearby. Here, the superscript refers to the quantum number of the corresponding vibration excited in the upper electronic state. ν_2 is the C=O stretch mode, and ν_4 is the out-of-plane deformation mode of formaldehyde. With the future improvement of the precision and acquisition of the new data from the rotational-state selection study, a comprehensive explanation for this interesting observation of the vibronic selectivity is expected. In any case it is clear that the value of Φ_H reaches a plateau of ∼0.3 at high excitation energies.

Rotational-State Selection

While studies of radiationless transitions from specific single vibronic levels of an "isolated" small polyatomic molecule are made to obtain a thorough understanding of the important primary photochemical processes, they cannot be complete without information concerning some of the key roles played by the rotational eigenstates. This has been well recognized in high-resolution molecular electronic spectroscopy.[22] Partic-

(20) (a) E. S. Yeung and C. B. Moore, *Appl. Phys. Lett.*, **21**, 109 (1972); (b) V. S. Letokhov, *Chem. Phys. Lett.*, **15**, 221 (1972); (c) R. V. Ambartsumian, V. M. Apatin, V. S. Letokhov, and V. I. Mishin, *Sov. J. Quantum Electron. (Engl. Transl.)*, **5**, 191 (1975); (d) J. B. Marling, *Chem. Phys. Lett.*, **34**, 84 (1975); (e) J. H. Clark, Y. Haas, P. L. Houston, and C. B. Moore, *ibid.*, **35**, 82 (1975).
(21) J. B. Marling, *J. Chem. Phys.*, **66**, 4200 (1977).

(22) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, New York, N.Y., 1966.
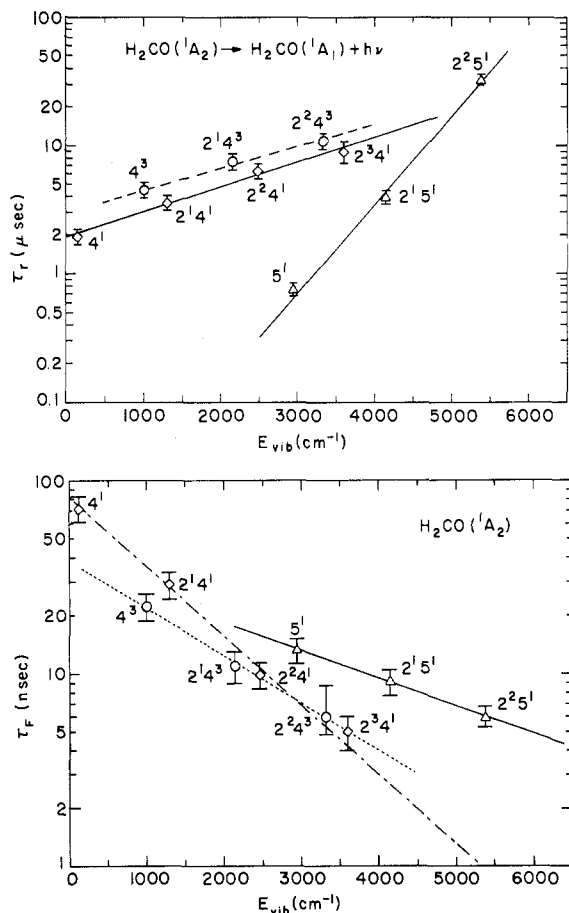
Figure 7. (a) The fluorescence decay time (τ_F) vs. E_{vib} in H_2CO ($\tilde{A}^1A_2$). (b) The radiative lifetime (τ_R) vs. E_{vib} in H_2CO ($\tilde{A}^1A_2$). Reprinted with permission from ref 5b. Copyright 1975 by *Chemical Physics Letters*.
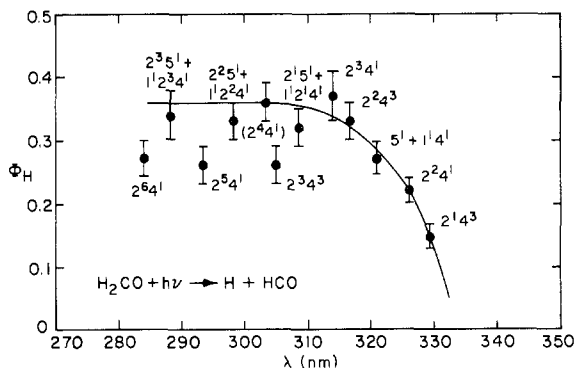
Figure 8. Quantum yield of H atom from the H_2CO photolysis vs. excitation wavelength.
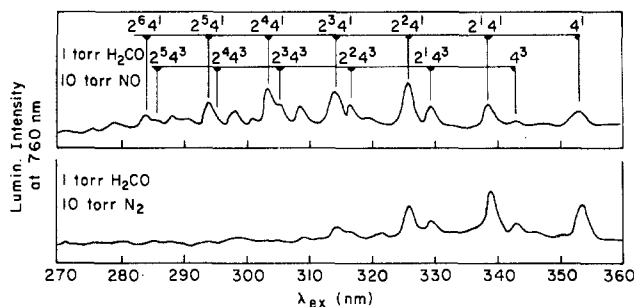
Figure 9. The red HNO* chemiluminescence excitation spectrum of the H_2CO/NO mixture (upper) is compared to the "background" fluorescence excitation spectrum of the H_2CO/N_2 mixture (lower). Reprinted with permission from ref 7a. Copyright 1976 by the American Institute of Physics.
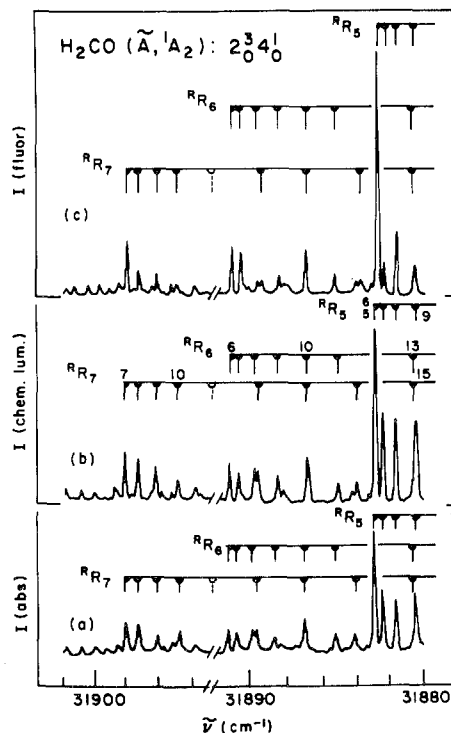
Figure 10. A portion of H_2CO spectra of the $2_0^3 4_0^1$ transition: (a) absorption spectrum with ordinate in absorbance unit; (b) red HNO* chemiluminescence excitation spectrum taken with the emission at 760 nm (1.0-torr $H_2CO/10$-torr NO); (c) blue H_2CO* fluorescence excitation spectrum taken with the emission at 380–500 nm (0.20-torr H_2CO). The rotational subbranch assignment as a near prolate top is $^{\Delta K}\Delta J_{K''}$ with J'' shown on top of the line. The line for $J'' = 11$ of $^R R_7$ is not shown. Reprinted with permission from ref 25. Copyright 1977 by the American Institute of Physics.

ularly with the use of tunable dye lasers, formaldehyde is ideally suited for such a study, since an enormous amount of the prerequisite information about singlet–triplet perturbation,[23] Coriolis coupling,[4e,24] Fermi resonance,[14e] and predissociation is already available from the high-resolution optical spectroscopy.

It is desirable to examine the values of Φ_F and Φ_H for each rotational level, since the variation of Φ_F reflects the change in the nonradiative processes ($S_1 \rightsquigarrow S_0$ or $S_1 \rightsquigarrow T_1$) as long as the value of τ_R remain the same and since the variation of Φ_H may further reflect the change in the efficiencies of the preceding radiationless processes. In order to evaluate these quantities accurately, it appears necessary to record the electronic absorption spectrum, the fluorescence excitation spectrum, and the HNO* chemiluminescence excitation spectrum at an equal spectral resolution. Such experiments have recently been carried out in our laboratory by continuously scanning the exciting laser frequency at a spectral bandwidth of 0.2 cm^{-1} and by a boxcar averager with the gated integrators which was used to record the appropriate signal ratios without delay (for absorption and fluorescence) or with a 2-μs delay (for chemiluminescence) from the laser pulse (1-μs width and 30 Hz).[25] A small portion of the results

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(24) (a) J. E. Parkins, H. G. Poole, and W. T. Raynes, *Proc. Chem. Soc., London*, 248 (1962); (b) J. E. Parkins, Ph.D. Thesis, University of London, 1962.

obtained for the rovibronic contour of the $2_0^3 4_0^1$ transition (3140 Å band in Figure 5), where congestion is minimum at the blue end, is shown in Figure 10,[25] since there are too many lines (~ 900) to show in a span of 320 cm^{-1}.

An inspection of Figure 10 and other results reveals that the intensity distribution in the chemiluminescence excitation spectrum is nearly identical with that in the absorption spectrum, but the intensity distribution in the fluorescence excitation spectrum is very much different. Several conclusions can be drawn. First, it is clear that the relative quantum yields of a hydrogen atom are constant for various rotational levels with rotational energies of 0–700 cm^{-1}. Second, the relative fluorescence quantum yields have a large variation. For example, the Φ_F values of $J' = 9$ of $K' = 7$ submanifold and $J' = 9$, 11, and 13 of $K' = 8$ submanifold are reduced by 4-fold. Since the perturbation mapped by Parkins[24b] in the $K' = 5 \sim 9$ stacks has a strong resonance at $J' = 11$ of $K' = 8$, the Coriolis perturbation is responsible for the loss of fluorescence. Finally, in contrast to the above perturbation effect, only small variations of the Φ_F values were observed among a large number of rotational levels populated by the $2_0^2 4_0^1$ transition at 3260 Å, despite the fact that the magnetic rotation spectrum and the Zeeman spectrum[23] show a strong S–T perturbation.

The above three surprising observations reveal some very crucial mechanistic insights. The $2^1 3^2 4^2$ and $2^1 4^2 6^2$ levels on the $\tilde{A}^1 A_2$ manifold which have been suggested to be the perturbing levels for the Coriolis interaction observed in the $2_0^3 4_0^1$ transition lie 100 and 130 cm^{-1} below $2^3 4^1$, respectively.[14e] Therefore, the large reduction of Φ_F observed for those perturbed rotational levels of $2^3 4^1$ must be due to a large enhancement of the $S_1 \rightsquigarrow S_0$ internal conversion rate through the intermediary participation of the above two resonant perturbing levels with nonoptical promoting modes. The lack of the S–T perturbation effect on Φ_F in the $2_0^2 4_0^1$ transition can be interpreted to mean that the suggested perturbing level, $1^1 2^2 4^1$ or $1^1 2^2$ of $\tilde{a}^3 A_2$ manifold, must have a lifetime considerably longer than the lifetime of the "pure" singlet $2^2 4^1$ level (~ 10 ns[5b]). Therefore, the triplet state must have a minor or negligible role in the photochemical mechanism for the $2^2 4^1$ level of the $\tilde{A}^1 A_2$ state, and despite the presence of a strong, localized S–T mixing the $S_1 \rightsquigarrow S_0$ internal conversion is probably the most important pathway for its radiationless transition. The observed constancy of Φ_H for all of the rotational levels of the $2^3 4^1$ level is consistent with a mechanism which requires both modes of photodecomposition, the radical (eq 4a) and the molecular processes (eq 4b), to occur from the ground-state manifold (S_0) following the $S_1 \rightsquigarrow S_0$ internal conversion process.[4] Whether or not this overall mechanism would apply to other vibronic levels needs to be tested.

Beyond "Rotation"

It is fascinating to think, chart, and speculate what lies ahead beyond the "rotation" barrier of photochemistry which has just been broken. However, the implication of the above conclusions should be exam-

ined first. One must realize that the existence of perturbation or mixing is a matter of degree, and one can capitalize on it to prepare or examine the "forbidden" states. In H_2CO ($\tilde{A}^1 A_2$), we have studied the optically forbidden triplet level ($1^1 2^2 4^1$) by exciting the S–T perturbed singlet level (of $2^2 4^1$) and the optically forbidden $2^1 3^2 4^2$ level by exciting the Coriolis perturbed $2^3 4^1$ level. Intramolecular vibrational energy flow in an "isolated" molecule is still a subject of much theoretical and experimental interest in unimolecular kinetics,[26] and Coriolis coupling and Fermi resonance are the mechanisms tractable to some experimental detail. However, we have found that when the Coriolis coupling is weak enough between some near-resonant rotational levels of the optically allowed vibronic states 5^1 and $1^1 4^1$ on the $\tilde{A}^1 A_2$ manifold of H_2CO, energy flow is prevented within its mean lifetime of ~ 10 ns.[27] Furthermore, the mechanism responsible for the efficient $S_1 \rightsquigarrow S_0$ internal conversion through a strong coupling between the nonoptical $2^1 3^2 4^2$ or $2^1 4^2 6^2$ level of $\tilde{A}^1 A_2$ and the resonant vibronic level of $\tilde{X}^1 A_1$ in H_2CO is still unknown, although some insight into the vibronic mechanism for the $S_1 \rightsquigarrow S_0$ internal conversion process in cyclobutanone has been gained, as discussed earlier.

The photochemical study of selected vibronic and rotational states suggests that the probability of extensive larger triplet mixing, Coriolis coupling, and Fermi resonance should be very high in larger aldehydes and ketones where the density of states is very high due to the presence of low frequency vibrations. This may be the reason for the predominance of the rapid $S_1 \rightsquigarrow T_1$ intersystem crossing in these molecules,[5a,9,28] in contrast to the prevalence of the $S_1 \rightsquigarrow S_0$ internal conversion in formaldehyde.[6d,25] The example of glyoxal is certainly an interesting one, for it is an intermediate case.[6e]

There are some obvious experiments which should shed the light in the topics described above. Briefly, lifetime studies would certainly complement the present study. The effects of the applied magnetic and electric fields on the photochemistry of the rotation selected states should be quite fascinating. The photofragment spectroscopy[29] of the vibration and rotation selected states should reveal very interesting dynamic details (particularly translational) when there are molecular perturbations involved, and it should be complementary to the emission spectroscopy. Although triatomic species can be studied more readily than the larger molecular species, the Doppler-free spectroscopy can greatly minimize the overlap problems of rotational lines as well as provide the lifetime information on the

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rovibronic levels. The study of collision-induced vibrational and rotational energy transfer and relaxation for an electronically excited molecule which can be followed through the emission spectroscopy[30] and the case involving the perturbation should be very interesting. We need further theories of radiative transitions to explain the enormous vibronic effects observed. Finally it must be emphasized that there have been a

few surprises, as discussed above, and this fact should clearly warn us that more of the interesting and significant surprises lie ahead.

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Temperature Dependence of Bimolecular Gas Reaction Rates

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In his classic 1889 paper[1] Arrhenius developed both the model and the basic equation still used today in explaining the temperature dependence of reaction rates. They might have remained merely suggested approximations were it not for the appearance a few years later of a remarkable achievement, the experiments of Max Bodenstein on $HI + HI \rightleftharpoons H_2 + I_2$, which raised the Arrhenius model (with A and E_A as constants) to canonical status for over half a century.[2-6]

By the 1960s two factors could and did change the situation. First, the temperature range over which elementary gas reaction rate constants could be measured was increased an order of magnitude by the refinement of flash photolysis, discharge-flow, and shock-tube techniques. Second, the number of complementary and intercomparable studies on related reaction systems became so great that critical evaluations of the data base became capable of sorting out experimental errors and characterizing nonlinear Arrhenius graphs.[7] Three classes of reactions are found to exhibit such behavior. One was recognized long ago, namely H or H^+ transfer reactions, where quantum-mechanical tunneling augments the classically allowed reaction rate and leads to low-temperature rates greater than a linear extrapolation of higher temperature data would suggest.[8] The second class is dissociation–recombination reactions. Here the temperature dependence of reaction rates is thoroughly enmeshed with the temperature dependence of energy-transfer rates, and the notion of elementary reaction becomes very blurred.[9] The third class is the bimolecular exchange reaction, and the discovery and interpretation of Arrhenius graph curvature for this class are our concern here.

The recognition that Arrhenius graph curvature for bimolecular exchange reactions had been characterized experimentally arose in connection with $OH + CO \rightarrow CO_2 + H$. Since this reaction is responsible for most of the conversion of CO to CO_2 in combustion, knowledge of its high-temperature rate constant is especially important. It appeared that the high-temperature and low-temperature data were simply inconcordant until Dryer, Naegeli, and Glassman[10] pointed out in 1970 that straightforward application of activated complex theory[11] reconciled both in terms of a curved Arrhenius graph (Figure 1).[10,12-15] For this reaction the contrast between the slight temperature dependence near room temperature and the rapid rise over 1000 K generates a dramatic pictorial effect. If the

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