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Presence of an Incubation Time in the Dissociation of CO

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band at 26 366 cm⁻¹ of the $n\pi^*$ state shows, at 4.2°K, the aforementioned linear Stark mixing effect, such that an electric field of 7.3×10^4 V cm⁻¹ directed along [110] of a single crystal causes a mean Stark splitting of 5.9 cm^{-1} . The observed pattern is consistent with that expected from the above treatment. The molecular orientation in the structure² leads us to values of between 09.8 and 07.8 D for $\Delta\mu$ on excitation to the $n\pi^*$ state. The known value of $\mu_0 = 2.98.^3$ This result is preliminary in that there remains an uncertainty in the electric field strength. The reduction of the dipole moment on excitation is quite similar to the value of $\Delta \mu = 0.86$ D for formaldehyde.⁴

This new method obviously has wide applicability to the absorption (ir and uv) and emission spectra of crystals and mixed crystals, such that it now becomes possible to obtain with relative ease the dipole moments of a number of different excited singlet and triplet states of a large class of molecules.

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² E. Fleischer, University of Chicago (unpublished results): We are indebted to Professor Fleischer for a preview of his x-ray analysis of the benzophenone crystal.

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(1964).

Presence of an Incubation Time in the **Dissociation of CO***

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A shock-tube study of the dissociation of shockheated carbon monoxide to determine its mechanism and rates has shown the presence of an incubation time which is in no way related to the coupling of vibration to dissociation discussed by Brau, Keck, and Carrier.¹

The observations are made in a 1.5-in. diameter shock tube behind the incident shock. The CO fundamental at 5 μ and C_2 at 0.5 μ are monitored with time resolutions of about 1 μs . The vibrational relaxation² is too fast to be resolved in these experiments. The temperature range lies between 6000° and 11 000°K.

A representative record is shown in Fig. 1. Under the conditions of these experiments the fall in the $5-\mu$ trace level is almost entirely due to the change in CO density, self-absorbtion being unimportant. It will be noted that the CO concentration falls slowly at first and then accelerates to a new rate. The time τ as defined on the trace is measured. τ decreases with increasing temperature and pressure. Plots of $\frac{1}{2} \log \tau^2 [M] [CO]$ versus 1/T where $\lceil M \rceil$ is the inert concentration gave an excellent correlation over a mixture range from



FIG. 1. The ordinate is $\tau p_1(\phi)^{1/2}$ where τ is in microseconds lab time, p_1 in torr, $\phi = 100 \times \text{fraction}$ of CO. The oscillogram shows a shock through 2% CO in Ne, $p_1=10$ torr. $U_s=3.90 \text{ mm/}\mu\text{sec}$ upper trace C2 emission, lower trace infrared CO emission.

0.02% to 10% CO. The traces also show C₂ rising during the incubation time, peaking shortly after the onset of the new dissociation rate and decaying. Care was taken to be quite certain the C_2 was not due to an impurity in the CO.

The two observations described immediately show that the CO dissociation is complex. The most likely scheme to explain the incubation time is

$$CO + M \underset{k_{1-}}{\overset{k_{1}}{\rightleftharpoons}} C + O + M, \qquad (1)$$

$$(C \text{ or } O) + CO \underset{k_2}{\overset{k_2}{\rightleftharpoons}} (C \text{ or } O) + CO^*,$$
 (2)

$$CO^* + M \underset{k_3}{\overset{k_3}{\rightleftharpoons}} C + O + M, \qquad (3)$$

where CO* implies any or all of the triplet states of carbon monoxide which dissociate into ground-state atoms. These states all lie between 6 and 8 eV with respect to the ground state.

The C_2 appearance and decay is due to reactions of the type

$$C + CO \underset{k_{-}}{\overset{k_{4}}{\rightleftharpoons}} C_{2} + O, \qquad (4)$$

$$C_2 + \underset{k_{5}}{\overset{k_5}{\longleftrightarrow}} C + C + M.$$
 (5)

Analytical solutions to this set of equations will not be attempted.

We assume that Reaction (3) is much faster than (1), and at the end of the incubation time (2) is in local equilibrium so that τ is the time required to build up an equilibrium population of CO^* via (2). Thus we get $\tau \approx [CO]K_2/[C][CO]k_2$, where K_2 is the equilibrium constant and [C] is taken as indicative of either [C] or [O]. During the incubation time the buildup of [C] from (1) will be approximately linear with time and at time τ , [C] \approx [CO][M] $k_1\tau$ and we get τ^2 [CO][M] \approx K_2/k_1k_2 , and we expect $\frac{1}{2} \log \tau^2$ [CO] [M] versus 1/T to give an activation energy approximately that involved in k_1 . The value found is 270 ± 30 kcal/mole whereas $D_0(CO) = 256$ kcal/mole. If [C] \approx [O], a similar argument may be made for C_2 instead of CO^* .

Attempts have been made to observe the radiation involved with the triplet states, but unfortunately the spectrum is dominated by C₂ and CN (the nitrogen being present as a minor impurity), and the results were inconclusive.

The presence of C_2 indicates that the shuffle reactions like those found in air chemistry³ are important. It is evident that the final decay rate of CO includes contributions from Reactions (1), (3), and (4). Estimates made with the Keck-Carrier theory of dissociation^{4,5} indicate that k_3 - and k_5 - may be ten times faster than k_1- .

A much fuller account of this work including a full numerical integration of the rate equations will be shortly submitted for publication.

* Supported by Ballistic Systems Division Contracts AF 04(694)-983 and AF 04(694)-690; and ARPA Contract DA-01-021-AMC-12 005Z) (part of Project DEFENDER). ¹ C. A. Brau, J. C. Keck, and G. F. Carrier, Phys. Fluids 9, 1825 (1066)

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Radiation Damping of Exciton States

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Silbey's interesting conclusion¹ that exciton states in molecular crystals are not radiation damped is unexpected because weakly coupled pairs of emitters are known to be damped,² and there is no reason to think that a crystal formed of a finite number of molecules will be different in so fundamental a way. We have reconsidered the problem from another point of view. If we follow Silbey's model of quantizing exciton and radiation fields in the same small volume, we agree with his result, which is that an exciton mode can couple to one mode only of the radiation field, and there is no damping. Quantization in the same volume is not, however, necessary in the problem and leads to other difficulties. We now write the Hamiltonian

$$\mathbf{H} = \mathbf{H}_{0} + \mathbf{H}_{rad} + \mathbf{V},$$

$$\mathbf{V} = -\sum_{p} \mathbf{q}_{p} \cdot \mathbf{E}_{p} \mathbf{I},$$
 (1)

where the terms are, respectively, the sum of the free molecule Hamiltonians, the free field Hamiltonian, and the interaction between field and charges in the dipole approximation. q_p is the dipole moment at site p and $\mathbf{E}_{n^{\perp}}$ the transverse component of the electric field of the radiation at the same point. In the form (1), which follows the proposal of Power and Zienau,³ the interaction V includes the intermolecular interaction as a second-order coupling via the radiation field.

A calculation of the damping of an exciton state of wave vector \mathbf{k} , defined in (2), can be made by the Heitler-Ma method4:

$$\Psi(\mathbf{k}) = N^{-1/2} \sum_{p} \exp(i\mathbf{k} \cdot \mathbf{p}) \phi_{p},$$
$$\phi_{p} = \psi'_{p} \prod_{q \neq p} \psi_{q}.$$
(2)

 ψ and ψ' are ground- and excited-state molecular wavefunctions in a crystal of N molecules, and the two expressions (2) are the delocalized and localized exciton functions, respectively. The initial state for the damping calculation is a crystal state of wave vector ${\bf k}$ and no photons. In order to recover the intermolecular contribution to the energy of this state (as a self-energy) as well as the radiation damping, it is essential on the one hand to include as final states both the no-exciton single-photon ground state and the two-exciton singlephoton states and on the other to treat the quantization volumes as independent. The result is that the initial time development of the amplitude of the k exciton state is given by (3),

$$b_{\mathbf{k}}(t) = \exp(-i\Delta E t/\hbar) \, \exp[-(\gamma + \gamma_0) t/\hbar]. \quad (3)$$

 ΔE is the required intermolecular contribution to the energy of the initial state,

$$\Delta E = \sum_{q}' \exp[i\mathbf{k}(\mathbf{p}-\mathbf{q})]I_{p,q},$$

 $I_{p,q}$ being the retarded dipole interaction between molecules p and q. γ_0 is the damping for the free molecule excited state ψ' , and γ a modulated damping