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Electron-Impact-Induced Phosphorescence of Benzophenone at Low Vapor Pressures

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Phosphorescences of benzophenone were measured at pressures between 0.4 and 2.2 Pa under electron impact. Emissions from vibrationally excited T_1 molecules were observed at lower pressures. Excitation mechanism by electron impact was discussed on the basis of excitation energy dependence.

Triplet states of benzophenone have been studied extensively. However, investigations have been restricted in the condensed phase, so far. Phosphorescence measurements in the gas phase are expected to provide important information concerning radiationless deactivation in isolated molecules or collision-induced relaxation processes. In the present study, benzophenone phosphorescences were measured at low vapor pressures using electron impact excitation in an attempt to obtain such information.

Experimental apparatus for the measurements of phosphorescences by electron impact have been described elsewhere.1) The optical band-pass for the luminescence measurements was 1 nm for spectra and 2 nm for decay curves and excitation functions. Benzophenone and n-hexane were distilled under reduced and normal pressures, respectively. The latter compound was used as foreign gas. The pressure was monitored using a Daia IT-40P ionization gauge, which was calibrated against an MKS Baratron absolute pressure gauge.

Figure 1a depicts a time-resolved emission spectrum of benzophenone at 1.2 Pa excited with 60-eV pulsed electron beam. The excitation duration, delay, and aperture times were 100, 10, and 100 μs, respectively. Spectrum measured with a lower electron energy of 25 eV was found to be very similar to that in Fig.1a. The spectrum exhibits prominent peaks at ≈390, ≈416, ≈447, and ≈481 nm, respectively. This spectrum is similar in shape to that of benzophenone phosphorescence measured under optical excitation in the rigid matrix at 77 K,2) apart from the facts that there is an additional weak peak at 390 nm and that each band has a rather large width. We assigned the present spectrum as that of benzophenone phosphorescence. Prominent peaks at 416, 447, and 481 nm were assigned as the 0-0 band and progressions in the C-O stretching mode, respectively. The 390 nm peak was assigned as phosphorescence from vibrationally excited T_1 state (hereafter abbreviated as VET) as will be shown below. To our best knowledge, this is the first observation of benzophenone phosphorescence excited with electron impact. Benzophenone phosphorescence at such a low pressure has not been reported yet.

Spectrum at pressure as low as 0.46 Pa (Fig.1b) is different from that of Fig.1a in that the band widths of respective prominent peaks are broadened and diffused and that 390 nm band is stronger. The effects of fragment emissions must be negligible since we measured the spectra with a delay time as long as 10 μs. Such changes of spectrum with decreasing pressure are very similar to those in the cases of benzaldehyde[3)] and acetophenone,[4)] and were ascribed to the occurrences of phosphorescence emissions from VET's at lower pressures. Such phosphorescence emissions constitute groups of sequence bands around prominent peaks, which make spectrum diffuse. At higher pressures, emission bands due to VET's are quenched owing to collision-induced vibrational relaxation. Spectrum of Fig.1a exhibits still diffused peaks and 390 nm band, indicating that pressure of 1.2 Pa is not high enough to suppress emissions from VET's. The band at 390 nm was assigned as emission from the VET with the excitation of one quantum of C-O stretching mode since this band is strong only at low pressures and since the energy seperation of 1600 cm^{-1} between this band and the 0-0 band is close to the energy of a fundamental C-O stretching vibration, 1650 cm^{-1}, in the ground state, which has been measured in benzophenone crystal by Udagawa et al.[5)] These authors also measured $T_1 \leftarrow S_0$ absorption and found an intense band at 1525 cm^{-1} above 0-0 energy, which they did not assign. This band can be assigned as transition to the VET with the excitation of one quantum C-O stretching mode.[6)] The present value of ≈1600 cm^{-1} for the energy of C-O vibration of the T_1 state approximately agrees with that in Ref.5, since large errors may be involved in the present study due to diffusness and relatively large band-pass of the spectrum in Fig.1.

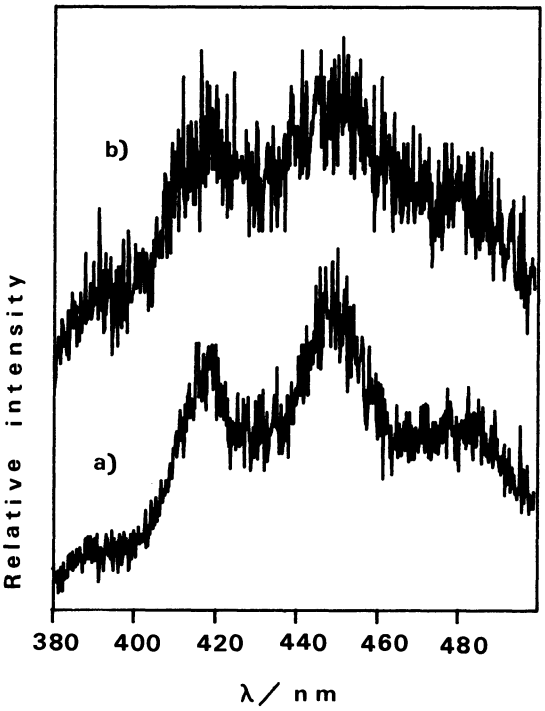

Fig.1. Time-resolved emission spectra of benzophenone: a) at 1.2 Pa; b) at 0.46 Pa.

Phosphorescence decay curves were measured at 416 and 390 nm as functions of pressure. At 416 nm decay curves were found to be non-exponential. We ascribed these non-exponential decays to phosphorescences from VET's. The decay curves were analyzed using Marquardt method.[7)] Residual and time-correlation plots indicate that observed decays are well expressed in terms of biexponential functions. The long-lived component was assigned as phosphorescence from thermalized T_1 state and the short-lived one as phosphorescences from VET's since the latter components become weaker at higher pressures. Apparent biexponential decays at this wavelength may be due to the fact that those states which are responsible for the fast component have decay rates similar in magnitude with one another or that single VET makes dominant contribution to the short-lived component. Figure 2 displays pressure dependence of decay rates; k_s and k_f stand for long-lived and short-lived components, respectively. k_s was found to increase slightly with decreasing pressure. The pressure dependence of k_s can be ascribed to wall effect. The value of k_s is (7-9) x $10^2 s^{-1}$ and is larger than the value obtained in condensed phase at low temperature by a factor of more than 3.[8] This discrepancy between the present decay rates and those reported in the literature can be attributed to temperature and/or wall effect. k_f, on the other hand, is on the order of $10^4 s^{-1}$ and increases rapidly with increasing pressure. The pressure dependence of k_f is attributed to efficient collision-induced relaxation of VET's. At 390 nm, phosphorescence decay curves were also analyzed as biexponential. However, the slow component is weaker comparing with the fast one in this case, and errors involved in determining decay rate of k_s may be large. We assigned the long-lived component as normal phosphorescence (shoulder of the 0-0 band) and the short-lived one as phosphorescence from VET. At this wavelength the VET with the excitation of C-O stretching mode is considered to play a dominant role. The pressure dependences of k_s and k_f are also displayed in Fig.2. The value of k_s is ≈ 7 x $10^2 s^{-1}$, and that of k_f is (2-3) x $10^4 s^{-1}$. The latter decay rate increases with increasing pressure. This pressure dependence is also attributable to collision-induced quenching of the VET. The rate of increase of k_f is smaller at 390 nm than at 416 nm. This indicates that VET's with excitations of vibrational modes other than C-O stretching are responsible for fast decaying component at 416 nm.

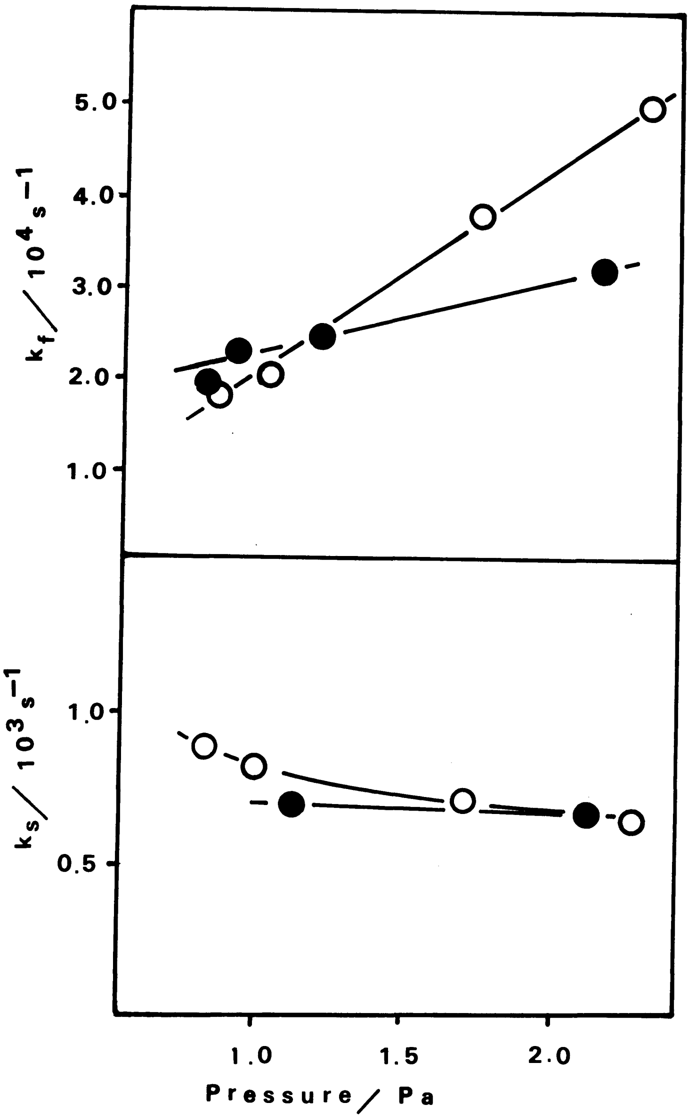

Fig.2. Pressure dependences of k_s and k_f: (○) at 416 nm; (●) at 390 nm.

Phosphorescence excitation function was measured at 416 nm at the pressure of 0.4 Pa in order to investigate excitation mechanism by electron impact. It exhibits an intense band at energies 6-20 eV, which has a rather complex structure, and a weak, broad band having a maximum around 60 eV. The lower-energy band may be attributed either to core-excited shape resonances or to non-resonant exchange mechanism, while the 60-eV band may be associated with pathways via singlet states followed by intersystem crossing.[9] It is concluded that in benzophenone triplet states are formed more efficiently with lower electron energies through resonances or by exchange mechanism. Measurements were also made at 390 nm at the same pressure (Fig.3b) in order to compare excitation mechanisms to zero-point level with those to VET's. The excitation function at 390 nm is similar in shape to that at 416 nm; however, the band width in the energies 15-20 eV is narrower and high energy band is smaller at 390 nm. Currently, detailed measurements of excitation functions are being made in order to ensure these differences and to investigate possible differences of excitation mechanisms to zero-point level and to VET's.

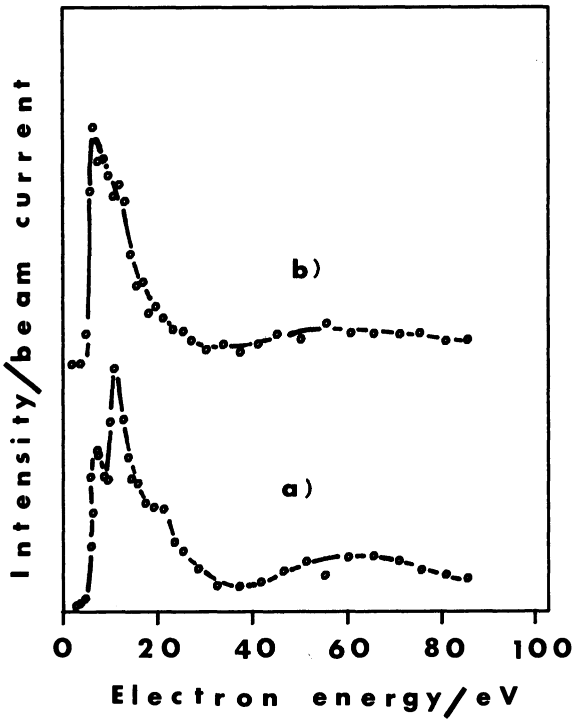

Fig.3. Phosphorescence excitation functions at 0.4 Pa:
a) at 416 nm; b) at 390 nm.

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