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Phosphorescence from Biacetyl and Benzophenone Surfaces by Collision with the T_1 State of Benzene

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Synopsis. Benzene molecules in the lowest-excited triplet state, T_1, were allowed to collide with biacetyl and benzophenone surfaces, and phosphorescence from the surface due to energy transfer from the T_1 state of benzene was observed. The possibility of application of this method to detection of metastable species is discussed.

The T_1 state of benzene (3.5 eV [1]) is known to transmit its excitation energy efficiently to the T_1 state of biacetyl in the gas phase causing phosphorescence [2]. The quantum yields of gas-phase phosphorescence are reported to be 0.23 and 0.9, and the energies of the T_1 states are 2.53 and 3.0 eV for biacetyl [3] and benzophenone [4], respectively. This phenomenon can be extended to a gas-solid system by use of a phosphor surface, instead of a phosphor gas, as an energy acceptor. Since such an energy transfer occurs exclusively on the surface and is expected to depend on the spin multiplicity, observation of phosphorescence from the surface has potential applicability, for example, to detection of low-lying metastable states. In the present note, we report observation of phosphorescence from biacetyl and benzophenone surfaces in collision with metastable benzene molecules.

Experimental

A schematic diagram of the apparatus is shown in Fig. 1. An effusive beam of benzene through a multichannel array A with a pushing pressure of 2—3 Torr (1 Torr=133.322 Pa) was excited by electron impact (2—20 eV) to the T_1 state [5]. The electron gun and the excitation region was magnetically shielded with μ-metal. Either biacetyl or benzophenone was deposited continuously on an alumimum surface cooled at 77 K from nozzle B. The metastable benzene molecules were allowed to collide on the phosphor surface after traveling 17 cm. The emission from the surface was detected through an interference filter having a band-pass of 10 nm. The filter was so chosen that the wavelength of the maximum transmittance of the filter coincided with that of the maximum intensity of the resulting emission, *i.e.*, band pass filters of 520-nm (Toshiba KL-52) and 440-nm (Toshiba KL-44) for biacetyl and benzophenone, respectively. Charged species produced concurrently were removed by an electrostatic deflector (see Fig. 1).

For measurement of the time dependence of the emission intensity, the molecular beam was excited by a pulsed electron beam with a pulse width of 70 μs and a repetition rate of 10 ms. The data were accumulated in a Hewlett-Packard 5480A multichannel analyzer for 2 h. For measurement of the excitation function, the emission intensity was recorded as a function of electron impact energy, where the electron beam was not pulsed. A part of the fluorescence from the benzene molecules produced in the excitation region was estimated and eliminated from the observed emission; for the purpose a quartz window, shown in Fig. 1, was placed on the beam path.

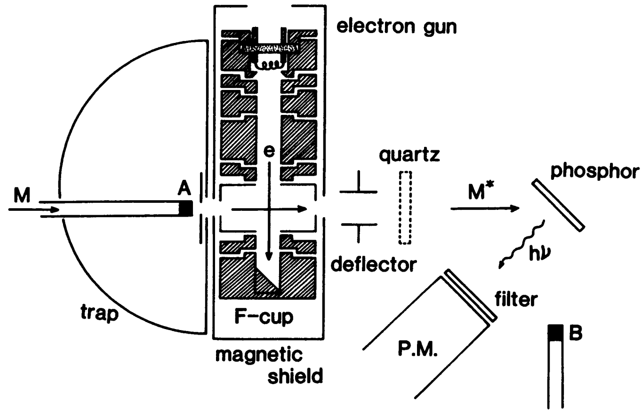

Fig. 1. A schematic diagram of the apparatus. A and B are multichannel slits for introducing benzene (M) and phosphor molecules, respectively, into the chamber. The emission from the phosphor surface is detected by a photomultiplier tube, PM. A quartz window is placed on the beam path when the contribution of stray light from the excitation region is estimated.

The signals at each impact energy were collected for 200 s, so that statistical errors were reduced to less than 6%. The absolute scale of the impact energy was calibrated by the threshold energy of the $N_2(C—B)$ transition [6].

Results and Discussion

The time-dependence curve of the emission from biacetyl surface is made of one sharp peak at $t \simeq 0$ ms and one broad peak at $t \simeq 0.6$ ms. The sharp peak arises from the photons produced in the excitation region, because (1) the peak appears at a time much shorter than the time of flight of the metastable molecules, and (2) only this peak is observed when no phosphor is deposited on the surface. Almost identical time dependence was obtained when benzophenone was used as a phosphor.

The emission forming the broad peak has maximum intensity at 520 nm for biacetyl and at 440 nm for benzophenone. Each wavelength coincides with that of the intensity maximum in the phosphorescence spectrum of the corresponding phosphor. Furthermore, the time of flight of the metastable benzene molecule agrees approximately with the time corresponding to the maximum intensity of the broad peak. These results indicate that the impinging metastable molecules to the target surface excite the phosphor by the $T—T$ energy transfer, which arises the broad peak, *i.e.*, the phosphorescence.

The shape of the broad peak is reproduced by

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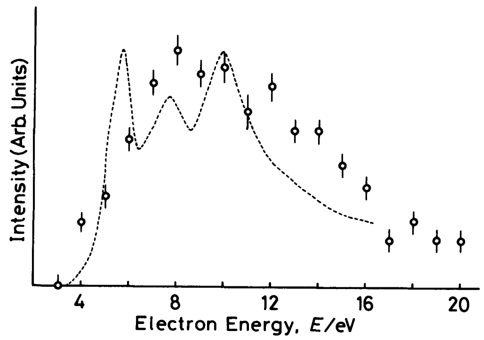

Fig. 2. Intensity of the phosphorescence (open circles) produced by collision of metastable benzene molecules on benzophenone surface (77 K) as a function of electron-impact energy. The broken line is the excitation function measured by Auger electron emission from sodium surface [7]. The ordinate is in arbitrary units.

assuming the velocity distribution of the metastable benzene molecules as

$$N(v) \propto v^4 \exp[-Mv^2/2kT], \quad (1)$$

where v and M are the velocity and the mass of benzene molecule, respectively. In addition, the phosphorescence is assumed to decay exponentially with a lifetime τ. The lifetime thus estimated, 1.0±0.2 ms, is much shorter than that for polycrystalline biacetyl (about 2 ms [2]). By optical excitation of polycrystalline biacetyl the excitation occurs in the bulk so that the measured lifetime corresponds to that of the phosphor molecules in the bulk. In contrast, the lifetime, τ, determined in the present measurement corresponds to that of the phosphor molecules on the surface, because the excitation energy of the T_1 state is transmitted directly to the phosphor surface.

Figure 2 shows the excitation function of the emission obtained by using benzophenone deposited on aluminum at 77 K. The excitation function rises in the vicinity of 3—4 eV, makes a broad maximum at 8—12 eV and falls off. This excitation function agrees qualitatively with that measured by Smyth *et al.* [7] by detecting Auger electron emission from sodium surface. In spite of the limited resolution ($\Delta E \simeq$ 2 eV) of the electron-impact energy in the present measurement, the general shape of the present excitation function provides another support that collision of the metastable benzene molecules is the main origin of the emission from the phosphor surface. A similar excitation function was obtained when biacetyl was used as a phosphor, where the signals were about 25% of those from benzophenone. The less intense signals from biacetyl is probably an indication that the phosphorescence quantum yield from biacetyl is about 25% of that from benzophenone [3,4]. On the basis of the reported cross sections for the formation of metastable benzene and $N_2(A^3\Sigma_u^+)$ molecules [8,9] and a comparison of the measured phosphorescence from metastable benzene molecules with that from the $N_2(A^3\Sigma_u^+)$ molecules, the phosphorescence yield from biacetyl surface is estimated to be on the order of 10^{-3}—10^{-4}. A more detailed study using a supersonic nozzle beam of metastable molecules is in progress [10].

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