A Specialist Periodical Report

Photochemistry

Volume 3

A Review of the Literature Published between July 1970 and June 1971

Senior Reporter

D. Bryce-Smith,

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ISBN: 0 85186 025 7

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The Chemical Society
Burlington House, London W1V 0BN

Introduction

With the appearance of Volume 3 of this Specialist Periodical Report, we begin to feel that 'Photochemistry' is becoming an established publication. The increase in length noted in Volume 2 has continued this year, but on a reduced scale, and we are optimistic that in the future we shall be able to stabilize at something like the present length without retreating from our present aim to cover essentially the whole of non-biological photochemistry in a single volume.

The general plan has been continued without significant alteration in this Volume, and we are glad to welcome Dr. B. H. Orger and Dr. D. H. Slater to the team of Reporters. Dr. Slater has contributed a section on Atmospheric Photochemistry which should be of interest to the growing number of chemists who are studying the photochemical aspects of air pollution. It is hoped to expand this section somewhat in Volume 4.

As always, we shall be grateful to be informed of any errors or major omissions which readers may discover.

D. B.-S.

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Part I

PHYSICAL ASPECTS OF PHOTOCHEMISTRY

1
Spectroscopic and Theoretical Aspects

The work reported in this section is categorized as in Volume 2 together with an additional section on Chemically Induced Dynamic Nuclear Polarization, a subject which is of increasing interest to photochemists. The restriction on the number of papers considered in Section 1 has been even more severe this year, and those selected for inclusion must inevitably represent a subjective selection by the authors from the very large number available. Nevertheless, it is hoped that those included are of interest to photochemists, and that those excluded on the grounds of space-saving are of less current general interest, although inevitably some of those excluded will have been of interest to particular groups and individuals working in the field.

1 Absorption Spectra and MO Calculations

The absorption spectrum of diatomic argon has been investigated in the 780—1080 Å region with a 6.65-m normal incidence vacuum spectrograph using the helium and argon continua as background sources. Nine discrete band systems were identified.[1] The analysis shows that the ground state is stable, has a dissociation energy $D_0^0 = 76.9$ cm^{-1}, and six vibration levels, v 0—5. A number of previous calculations of intramolecular potentials agree with these experimental results. Definite dissociation products are assigned for some of the upper states of these systems. A triplet potential surface for argon has been calculated,[2] and Wanner-type impurity excited states in liquid rare gases reported.[3]

It has been shown that the gross shifts in the spectrum of the Hg $^3P_1 \leftarrow {}^1S_0$ transition of Hg in solid rare gases can be correlated by considering the difference in the interaction potential between the lattice and the Hg atom in the $^3P_1$ and $^1S_0$ states, providing the distortion of the lattice caused by the Hg atom is taken into account.[4] In Ar, Kr, and Xe the spectrum can consist of three separate components. It was quantitatively shown that one component arises from relatively isolated Hg atoms, the other two from Hg atoms having nearest neighbour Hg atoms. This interpretation has been criticized,[5] and an alternative suggested in which

[1] Y. Tanaka and K. Yoshino, *J. Chem. Phys.*, 1970, **53**, 2012.
[2] J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, 1971, **54**, 3472.
[3] B. Raz and J. Jortner, *Chem. Phys. Letters*, 1970, **4**, 511.
[4] M. McCarty jun., *J. Chem. Phys.*, 1970, **52**, 4973.
[5] H. S. Freedhoff and W. W. Duley, *J. Chem. Phys.*, 1971, **54**, 3244.

the two additional absorption components arise from splitting of the $^3P_1$ state of Hg by the asymmetry of the crystal field caused by a vacancy adjacent to the Hg atom. The latter interpretation is itself subject to several criticisms.[6] The intensities of the two additional components relative to the main component depend on the Hg doping concentrations [3] as predicted by the Hg–adjacent-Hg hypothesis but not by the Hg–vacancy hypothesis. In addition, there is no obvious reason why the equilibrium concentration of a Hg–vacancy complex should greatly exceed the fractional concentration of vacancies in pure rare gases at equilibrium. On energetic grounds the reverse would be more likely. Since the equilibrium mole fraction of vacancies is about 0.015 at the triple point of Ar and Kr, and since for Ar the equilibrium value of about 10^{-4} can be attained rapidly at 50 K, it would be surprising if the ratio of substitutional Hg to Hg-adjacent vacancy exceeded 0.1, whereas at least this fraction is necessary to explain the observed relative intensities.

A semi-empirical treatment has generated potential energy curves of the hydrogen molecule in the ground $^1\Sigma_g$ and excited $^3\Sigma_u$ states.[7] A spectroscopic study of deuterium photolysis has been reported.[8]

Hartree–Fock (HF) electronic transition moments have been calculated [9] in both the position and momentum representations, and were presented as a function of the internuclear separation R for the BeH, MgH, OH, and SH (A–X) systems. The vibrational averages of these quantities were obtained and the results used to calculate some absorption band oscillator strengths. For the OH (A–X) system several independent experimental determinations of the 0–0 band oscillator strength have been reported in the literature, and the theoretical value of 20.6×10^{-4} differs from experiment by a factor of 2.5. Consideration of the united and separated atom limits and the region of the equilibrium internuclear separation for the states involved leads to an abbreviated discussion of the effect of correlation on the HF transition moments. HF transition moment calculations at a single value of R were also reported for the BH^+, AlH^+, HF^+, and HCl^+ (A–X) systems.

By means of a photoelectrical technique,[10] the absorption cross-section of the O_2 continuum in the region 2350—1814 Å and the absorption cross-section of CO_2 in the region 2160—1718 Å have been measured. The cross-section of the O_2 continuum is 3.8×10^{-24} cm^2 at 2350 Å; it slowly increases towards shorter wavelengths and reaches 10.7×10^{-24} cm^2 at about 1980 Å, then increases very rapidly and reaches 7.1×10^{-22} cm^2 at about 1814 Å. In the case of CO_2, numerous discrete bands were found overlapping a weak continuum in the wavelength region below 1980 Å. The absorption cross-section of the CO_2 continuum is about 2×10^{-24} cm^2

[6] M. McCarty jun., *J. Chem. Phys.*, 1971, **54**, 3245.
[7] A. B. Sannigrahi, *Indian J. Chem.*, 1970, **8**, 610.
[8] F. J. Comes and U. Wenning, *Z. Phys. Chem.* (*Frankfurt*), 1970, **70**, 139.
[9] W. H. Henneker and H. E. Popkie, *J. Chem. Phys.*, 1971, **54**, 1763; H. E. Popkie, *ibid.*, 1971, **54**, 4597.
[10] M. Ogawa, *J. Chem. Phys.*, 1971, **54**, 2550.

at 2100 Å; it gradually increases toward the shorter wavelength side, and reaches about 4×10^{-24} cm² at 2000 Å. The continuum rises rapidly at 2000 Å and its value is 1.19×10^{-20} cm² at 1718 Å.

Absorption coefficients of $^1\Delta_g O_2$ have also been measured in the far u.v.[11] Measured lifetimes of rotational and vibrational levels of electronic states of N_2 have been reported.[12] Vacuum-u.v. spectroscopy and photoelectron spectroscopy have been used to determine the electronic structure of NO_2,[13] and the results correlated with Gaussian orbital calculations. These results may be compared with those calculated by other workers.[14]

It has been demonstrated by photofragment spectroscopy that the long-accepted assignment of the main I_2 visible continuum as being almost entirely due to a transition to the $B\,0^+u(^3\Pi)$ state is incorrect. In reality, a transition to a $1u$ state, probably the $1u(^1\Pi)$ is of at least comparable, if not greater, importance.[15] An I_2 molecular beam was crossed with pulses of polarized light from a laser-pumped tunable dye laser, and the distribution of recoiling I atoms measured with a mass spectrometer as a function of flight time and of recoil angle measured from the electric vector of the light. The observed $B\,0^+u(^3\Pi) \leftarrow X\,0^+g(^1\Pi)$, and $1u \leftarrow X\,0^+g(^1\Pi)$ transitions are clearly separated both by flight time and recoil angle, as shown in Figure 1.

The upper panel shows the results of photolysis in the main I_2 visible continuum at 21 510 cm^{-1} with the polarization set so that the detector is at $-70°$ from the electric vector of the light in the laboratory (lab) co-ordinate system. This corresponds approximately to measurement perpendicular to the electric vector in a centre-of-mass (c.m.) co-ordinate system whose origin travels with the moving I_2 molecule. To a good first approximation, the c.m. to lab transformation simply rotates the angular distribution by an angle $\Theta = \arcsin c/u$, in which c is the original speed of the I_2 molecule and u is the c.m. speed of the recoiling I atom. The peak is at such short flight times that the dissociation must be to ground-state atoms, as all the photon energy available after breaking the I_2 bond is expressed as translational energy of the atoms. The recoil of the atoms predominantly perpendicular to the electric vector of the light indicates that the transition dipole moment is perpendicular to the internuclear axis (*i.e.* $\Delta\Omega = \pm 1$, and thus $\Omega = 1$ in the upper state). The only $1u$ states correlating with ground-state atoms are the $A\ 1u(^3\Pi)$ and $1u(^1\Pi)$. The $A\ 1u(^3\Pi)$ should lie lower and almost certainly corresponds, as in the usual assignment, to the weak long-wavelength bands and continuum. That this weak continuum indeed corresponds to a $1u$ state has also been confirmed by photofragment spectroscopy at 14 405 cm^{-1}. Thus, the peak shown in the

[11] M. Ogawa, *J. Chem. Phys.*, 1970, **53**, 3754.
[12] A. W. Johnson and R. G. Fowler, *J. Chem. Phys.*, 1970, **53**, 65.
[13] C. R. Brundle, D. Newmann, W. C. Price, D. Evans, A. W. Potts, and D. G. Streets, *J. Chem. Phys.*, 1970, **53**, 705.
[14] W. H. Fink, *J. Chem. Phys.*, 1971, **54**, 2911.
[15] R. J. Oldman, R. K. Sander, and K. R. Wilson, *J. Chem. Phys.*, 1971, **54**, 4187.

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