On the Structure of Ozone

D. M. Simpson

of quenching, or with an appreciable temperature coefficient if an energy of activation is the principal restrictive factor.

In continuation of work instigated by Professor R. G. W. Norrish on the factors influencing degradation of electronic excitation energy to thermal energy, we have investigated a quenching process of small cross section; the quenching of excited sodium by methane. Norrish and Smith[1] found that the cross section for the quenching of sodium atoms in the 3^2P state by methane is approximately 0.11×10^{-16} cm² at 130°C. We have carried out measurements at 585°C and at 615°C, using the method developed by Terenin[2] and by Winans[3] in which sodium atoms excited to the 3^2P state are produced by photo-dissociation of sodium iodide, the energy absorbed in excess of that required to produce dissociation going into kinetic energy of the sodium and iodine atoms. Nickel and cadmium condensed sparks have been used as sources of the radiation producing photolysis. The details of our experimental method resembled those of Winans.

Methane proved to be weakly quenching under our experimental conditions and in consequence cross sections have been calculated on the assumption that, before suffering quenching, sodium atoms attain velocities characteristic of the temperature of the quenching gas. The values for the cross sections evaluated in this manner are 0.19×10^{-16} cm² for 585°C and 0.16×10^{-16} cm² for 615°C. (There was no significant dependence of quenching ratio on the nature of the spark.) Because of the difficulties in photometry associated with the presence of a perceptible background of radiation and the low intensities of the radiation from the sodium, and because of the small extent of the quenching, these values are probably not significantly different and cannot be considered alone to indicate the magnitude of the temperature coefficient. However, taken in conjunction with the value 0.11×10^{-16} cm² obtained by Norrish and Smith by the resonance method at 130°C, they do indicate that the temperature coefficient for quenching by methane is very small.

If the only restrictions on the occurrence of quenching are the approach of the centers of the sodium atom and methane molecule to within about 4×10^{-8} cm and an activation energy (localized in two square terms), then a change in temperature of the system from 130°C to 585°C should be accompanied by a change in cross section from 0.11×10^{-16} cm² to approximately 4.5×10^{-16} cm². Our results consequently indicate that an activation energy is not the important restrictive factor.[4] They do not, however, allow separate evaluation of the factors which lead to the small cross section.

The methane was prepared by the action of a zinc copper couple on a solution of methyl iodide, and was purified by passage through fuming sulfuric acid, over heated copper oxide, and by several distillations in vacuum. A portion of the gas subjected to a second purification showed no significant change in quenching properties.

[1] Norrish and Smith, Proc. Roy. Soc. London A176, 295 (1940).
[2] Terenin, Zeits. f. Physik 37, 98 (1926).
[3] Winans, Zeits. f. Physik 60, 631 (1930).
[4] K. J. Laidler, J. Chem. Phys. 10, 34 (1942).

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THE shape of the ozone molecule is still a subject for controversy. Adel and Dennison,[1] from investigations of the rotational fine structure of the infra-red bands, considered that they had obtained conclusive evidence for an acute-angled structure, and this seemed supported by the bond-energy calculations of Glockler and Matlack.[2] More recently Eberhardt[3] has shown that the bond energies can equally well be interpreted on the basis of a wide-angled model with dimensions given by the electron-diffraction investigations.[4] It is the purpose of the present note to indicate that the interpretation of the infra-red bands given by Adel and Dennison is not unique, and that their experimental data are not incompatible with a wide-angled structure.

Adel and Dennison suggest: (a) that the strong band at 705 cm⁻¹ is near perpendicular in type, with a coarse rotational spacing ~5.7 cm⁻¹ and subsidiary fine structure, so that the change in electric moment for this vibration must be along the middle axis of inertia; (b) that since both the strong bands at 1043 and 2108 cm⁻¹ have Q branches and a rotational spacing of ~1 cm⁻¹, and since their appearance is very different from that of the 705-cm⁻¹ band, they must both be near parallel bands with change in electric moment along the least axis of inertia.

Taken together, these arguments indicate that if the three strongest regions of absorption correspond to the three fundamental frequencies, that since 1043 and 2108 cm⁻¹ are near parallel bands and 705 cm⁻¹ is near perpendicular, the assignment to ν_1, ν_2, and ν_3, respectively, follows; moreover, the molecule must be acute-angled, the least axis of inertia coinciding with the symmetry axis. The moments of inertia may then be calculated from the observed rotational spacings, and the apical angle so derived (34°) is in good agreement with that obtained from the fundamental frequencies (39°) using a central force field.[5]

From the published curves for the bands at 1043 cm⁻¹ and 2108 cm⁻¹,[6,7] it is seen that the latter has a pronounced Q branch, while the former, at least under low dispersion, has none. The dissimilarity of the contours is striking. It should also be noted that the published curves were not obtained under ideal conditions, the band at 1043 cm⁻¹ is overlaid with carbon dioxide absorption, that at 2108 cm⁻¹ was observed using a specimen admittedly contaminated with nitrogen pentoxide, a substance which absorbs in the same region.[8] The fine structure observed, therefore, cannot be due entirely to ozone. There is thus some justification in criticizing Adel and Dennison's conclusion that both 1043 and 2108 cm⁻¹ are near parallel bands. Further, unless both are near parallel bands, the molecule is not necessarily acute-angled and their interpretation of the rotational fine structure is not unique.

For the wide-angled model, the middle axis of inertia coincides with the symmetry axis. A_1 bands (eg., ν_1, ν_2) have a doublet structure, B_1 bands (e.g., ν_3) a Q branch. For this

model the observed spacing of the rotational fine structure is the true spacing for both A_1 and B_1 bands, in spite of the identity of the oxygen nuclei with their zero nuclear spin. It is clear that the 705-cm^{-1} absorption corresponds to an A_1 band; the change in electric moment for the 2108-cm^{-1} frequency is probably along the least axis of inertia (on account of its pronounced Q branch), making it a B_1 band. The moments of inertia may be calculated from the observed spacings 5.7 and 1 cm^{-1}, using the method of Adel and Dennison. The second column of Table I shows the results of these calculations for the wide-angled model. The third column gives the observed electron-diffraction data for the bond length and apical angle, together with the moments of inertia derived from them. Adel and Dennison's results for the acute-angled model are included for comparison in the fourth column.

The agreement between the electron-diffraction data and the present calculations is moderately good. Exact agreement would not be expected. It should be emphasized that these calculations are not very accurate; the formulae used to obtain the moments of inertia from the line spacings are rough approximations—modifications of those for a symmetrical top; further, the observed line spacings are not known precisely (particularly that for the near parallel band at 2108 cm^{-1}), and the moments of inertia are rather sensitive to small changes in these spacings.

The electron-diffraction data may be used to calculate corresponding line spacings, which are found to be 0.8 and 9.0 cm^{-1}, respectively, for near parallel and near perpendicular bands. Reduction in apical angle or increase in bond length both lead to a decrease in the line spacing of near perpendicular bands without seriously affecting that of near parallel bands. Small changes of both angle and bond length would be sufficient to give much closer agreement between the calculated and observed line spacings, though such changes would be larger than the published limits of error.

It is clear from the above considerations that the fine structure observed in the infra-red absorption of ozone may be interpreted on the basis of a wide-angled model. A detailed comparison of the molecular dimensions derived from electron diffraction and the fine structure of the infra-red bands must be reserved until the complete analysis of this fine structure has been carried out. It will then be possible to consider whether in fact the electron-diffraction data require modification.

For the wide-angled model, if any permutation of the three strongest bands (705, 1043, and 2108 cm^{-1}) is chosen for the fundamental frequencies, it is impossible to obtain sensible values of the force constants from a valency force field. The only other suitable frequency is at 1740 cm^{-1}, a weak band of uncertain contour observed to date only under low dispersion.[5] If a plausible value of the O—O force constant is to be derived, consistent with the observed bond length of 1.26A, it may readily be shown that 1740 cm^{-1} must be assigned to ν_3. Since 2108 cm^{-1} cannot be an A_1 band because of its pronounced Q branch, it follows that 1043 and 705 cm^{-1} must correspond to ν_1 and ν_2, respectively. This interpretation, first proposed by Penney

TABLE I.

	Present work error ±20%	Electron diffraction	Adel and Dennison error ±20%
I_A	60.5 ×10^{-40} g cm^2	73.16 ×10^{-40} g cm^2	64 ×10^{-40} g cm^2
I_B	52.0 ×10^{-40} g cm^2	67.56 ×10^{-40} g cm^2	50 ×10^{-40} g cm^2
I_C	8.5 ×10^{-40} g cm^2	5.60 ×10^{-40} g cm^2	14 ×10^{-40} g cm^2
O—O side	1.2A	1.26 ±0.02A	1.8A
O—O basal	2.0A	2.24 ±0.06A	1.0A
2α	110°	127 ±3°	34°

and Sutherland[9] has its difficulties, in particular, unreal values of the deformation force constants are obtained for most types of force field.[10] Calculations using a valency force field with $\nu_2 = 705$ cm^{-1} $2\alpha = 127°$ and a bond force constant of 9.53×10^5 dyne/cm (derived from Badger's relationship, the O—O distance being 1.26A) indicate that a small change in the frequency of either ν_1 or ν_3 would be sufficient to make the deformation force constant real. The unreality of the force constants as calculated directly from the observed frequencies, therefore, cannot be considered as a serious objection to this interpretation, which has the merit that it is in agreement both with the dipole moment[11] and the electron-diffraction data.

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Acta Crystallographica

A NEW journal of crystallography, Acta Crystallographica, sponsored by the recently formed International Union of Crystallography, will start publication in January, 1948. The journal is intended to take the place of the former Zeitschrift für Kristallographie, but in recognition of the rapid development of structural studies in recent years it is intended that it shall be somewhat broader in its scope and that it shall concern itself with all those physical and chemical properties of matter intimately connected with atomic arrangement. The journal will thus be one touching the interests of the chemist, the physicist, the metallurgist, the mineralogist, and even the biologist.

The journal will be published by the Cambridge University Press under the editorship of Professor P. P. Ewald, a former editor of the Zeitschrift für Kristallographie, and a panel of regional co-editors. It will appear in six issues a year. The annual subscription will be $10.00 or £2. 10.0., and by courtesy of the American Institute of Physics arrangements have been made for subscribers in