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Detection of the HO2 Radical by Mass Spectrometry

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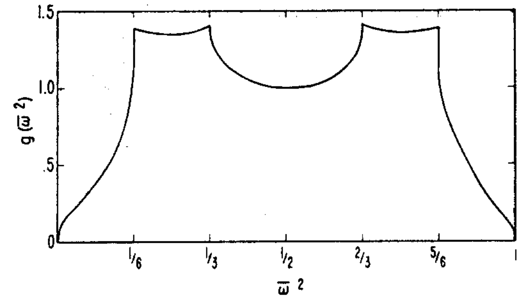

FIG. 2. Frequency distribution, $\sigma=\frac{1}{4}$.

with the one obtained for nearest neighbor interaction with vibrations in a "fourth dimension".[2]

Since the above discussion shows all the general features of the distribution, the actual calculation of g for any given value of σ requires numerical evaluation of Eq. (3) at only very few points. An example, $\sigma=\frac{1}{4}$, is shown in Fig. 2.

We wish to thank Mr. D. A. Patterson for checking certain calculations.

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[1] G. F. Newell, J. Chem. Phys. (to be published).
[2] W. A. Bowers and H. B. Rosenstock, J. Chem. Phys. 18, 1056 (1950).
[3] H. B. Rosenstock and H. M. Rosenstock, J. Chem. Phys. (following letter).
[4] L. vanHove, Phys. Rev. 89, 1189 (1953).

Vibrations of a Simple Cubic Lattice. II

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(Received August 2, 1953)

As in the preceding letter,[1] consider a simple monatomic cubic lattice but assume that the forces are central and non-negligible down to third nearest neighbors, i.e., set

$$V=\left[\tfrac{1}{2}\alpha\sum_{\substack{\text{nearest}\\ \text{nbrs.}}}+\tfrac{1}{2}\beta\sum_{\substack{\text{2d nearest}\\ \text{nbrs.}}}+\tfrac{1}{2}\gamma\sum_{\substack{\text{3d nearest}\\ \text{nbrs.}}}\right]d^2,$$

d being the distance between two atoms. By expanding about equilibrium positions keeping only the first nontrivial (i.e., quadratic) terms, we obtain, in the usual manner, the secular equation

$$\Delta(\omega^2;\sigma,\tau;c_1,c_2,c_3)=0, \tag{1}$$

which determines the frequencies ω^2. Explicitly, Δ is a 3×3 determinant with diagonal elements $f_{ii}=1-c_i+\sigma(2-c_ic_j-c_ic_k)+\tau(1-c_ic_jc_k)-m\omega^2/2\alpha$ and off-diagonal elements $f_{ij}=s_is_j(\sigma+\tau c_k)$. Here $\sigma=\beta/\alpha$, $\tau=4\gamma/3\alpha$, $s_i=(1-c_i^2)^{\frac{1}{2}}$ and c_i is defined in I. (1), begin a cubic in ω^2, may be solved for ω^2 by elementary algebra to give three solutions

$$\omega^2=\omega_1^2,\ \omega^2=\omega_2^2,\ \omega^2=\omega_3^2, \tag{2}$$

but the expressions $\omega_i^2=\omega_i^2(\sigma,\tau,c_1,c_2,c_3)$ are irrational and rather complicated and therefore of little use in finding the distribution of frequencies. One is therefore led to search for values of σ, τ such that one or more of the ω_i^2 become rational.

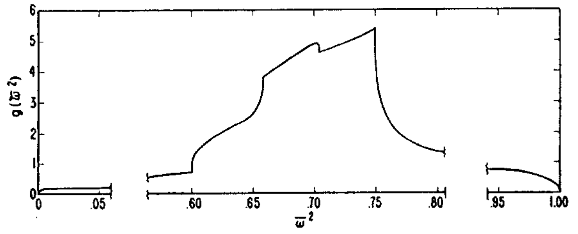

FIG. 1. Frequency distribution. The singularities are at $\bar{\omega}^2=6/10$, $2/3$, $(35+10^{\frac{1}{2}})/54$ and $3/4$. To save space, the regions $0.05<\bar{\omega}^2<0.55$ and $0.85<\bar{\omega}^2<0.95$, in which the function is smooth, are not shown.

It is known that this happens in the mathematically simple and physically trivial case $\sigma=\tau=0$. We find that the only other case in which this happens is $\sigma=3/7$, $\tau=2/7$ (meaning $\beta/\alpha=6/14$, $\gamma/\alpha=3/14$). We then obtain

$$\omega_1^2=(2\alpha/7m)\Big[21-\sum_i c_i-4\sum_{i>j}c_ic_j-6c_1c_2c_3\Big] \tag{3}$$

but ω_2^2 and ω_3^2 remain irrational,

$$\omega_{2,3}^2=(2\alpha/7m)\Big[12-3\sum_i c_i-\sum_{i>j}c_ic_j \pm\Big\{\tfrac{1}{2}\sum_{j\neq i\neq k}(1-c_i)^2(c_j-c_k)^2\Big\}^{\frac{1}{2}}\Big]. \tag{4}$$

We are unable to compute the distribution of the ω_2^2 and ω_3^2 branches. The distribution of the ω_1^2 branch can, on the other hand, be obtained with the use of (3) in Eq. (2) of I. As in I, the first two integrations can be done in closed form, leading to elliptic integrals, and a study of the behavior of these in the $(c-\omega_1^2)$ plane enables one to locate the points of interest (i.e., the singularities) of the distribution function and to infer its behavior there. (The nature and location of the singularities may also be understood from the connectedness of the surfaces of constant ω_1^2 in (X_1, X_2, X_3) space as given by (3).) The calculation of the distribution may then be completed by numerical integration of the last remaining integral at a very few points. The distribution is exhibited in Fig. 1. The function is very small from 0 to 0.60; more than half of the frequencies seem to be concentrated in the region $0.60<\bar{\omega}_1^2<0.80$. It is continuous throughout its range and has square root behavior at each end point; in the neighborhood of each of the other four singular points, it shows square root behavior at one side and is linear on the other, in agreement with van Hove's[2] general results.

We wish to thank Dr. W. A. Bowers and Dr. G. F. Newell for helpful discussions.

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[1] H. B. Rosenstock and G. F. Newell, J. Chem. Phys. 21, 1607 (1953) (preceding letter), henceforth referred to as I.
[2] L. van Hove, Phys. Rev. 89, 1189 (1953).

Detection of the HO_2 Radical by Mass Spectrometry*

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(Received June 29, 1953)

ALTHOUGH the HO_2 radical has been postulated as an intermediate in many chemical reactions, no direct experimental proof of the existence of this radical has been presented to date. This letter reports the mass spectrometric detection of the HO_2 radical in the gas phase reaction of hydrogen atoms with oxygen molecules.

The experimental arrangement which we have employed is shown in Fig. 1. Oxygen mixed with an inert gas, which serves both to stabilize the gas flow and to deactivate molecules, is in-

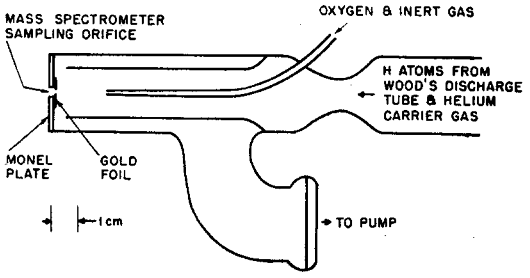

FIG. 1. Experimental arrangement.

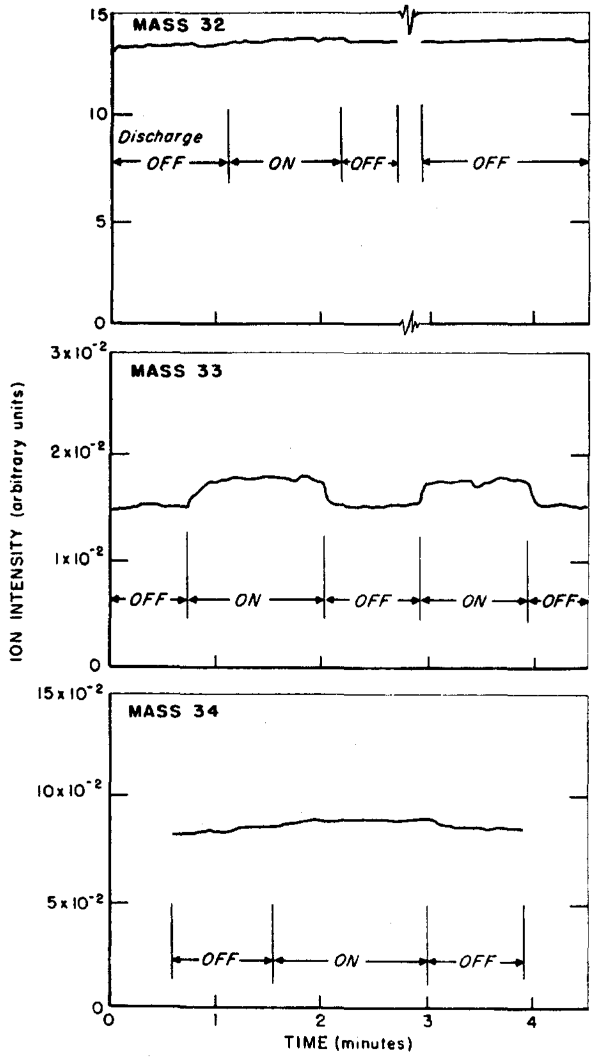

FIG. 2. Ion intensities of masses 32, 33, and 34 at 60 volts electron energy for the reaction of hydrogen atoms with oxygen molecules. The ordinate scale for mass 32 should be multiplied by 1.6. Measurements were made in the sequence: mass 32, mass 33, mass 34, followed by a check on mass 32 indicated by the break in the abscissa.

jected into the center of the atomic hydrogen stream. A constriction in the glass system prevents back diffusion of oxygen molecules into the discharge tube. The reaction products enter a special mass spectrometer, previously described,[1] which employs a molecular beam sampling system. The inlet orifice is a pinhole 0.010 cm diameter in a foil 0.0025 cm thick.

The ion intensities at the oxygen isotopic masses 32, 33, and 34 were observed to determine if any HO_2 was being produced. Measurement of mass 34 intensity is necessary to rule out isotopic diffusion effects and to monitor the production of H_2O_2 which yields some HO_2^+ as an ionization fragment. At pressures of a few cm of Hg. we have found that the intensity of the mass 33 peak increased abruptly when the discharge tube was turned on, while under the same conditions the ion intensities at masses 32 and 34 remained substantially constant. In Fig. 2 are shown tracings of the records for a run at a pressure of 3.7 cm of Hg when CO_2 was mixed with the oxygen. The gas velocity in the reaction region was about 500 cm/sec. Generation of hydrogen atoms in the discharge tube in clearly correlated with a stepwise rise in the mass 33 ion intensity well above the $O^{16}O^{17}$ isotopic level. In this experiment a slight rise in the 34 peak, which might be due to H_2O_2, was observed with the discharge on. The contribution of such a small amount of H_2O_2 to the mass 33 peak would, however, be less than the noise level. Increases in mass 33 intensity have similarly been observed with argon and helium serving as the inert gas mixed with the oxygen. In 16 out of 18 observations made under various experimental conditions no increase in the 34 peak was observed, while in all cases an increase, averaging 9.2±2.1 percent, in the 33 peak was obtained.

The ion intensity at mass 33 cannot come from any impurity in the system as turning off the oxygen supply completely removes the 33 peak. The presence of HO_2 when operating the system at a few cm pressure is in accord with the prediction that HO_2 is formed in intermolecular collisions:

$$H+O_2+M\rightarrow HO_2+M, \qquad (1)$$

where the third body, M, removes excess energy.

Some rough values of ion intensities in one of the experiments are given in Table I. It will be observed that considerable amounts of OH and H_2O are produced in the reaction. The OH is formed presumably by the reaction,

TABLE I. Ion intensities at 60 volts electron energy. Total pressure =3 cm, CO_2:O_2 ratio 2:1. The OH intensity has been corrected for the contribution from H_2O.

Component	Ion intensity (arbitrary units)
H	0.45×10^{-2}
H (O_2 off)	1.42×10^{-2}
H_2	18.2×10^{-2}
OH	3.0×10^{-2}
H_2O	9.2×10^{-2}
HO_2	0.14×10^{-2}
O_2	11.9
He	6.4

$$HO_2+H_2\rightarrow OH+H_2O, \qquad (2)$$

since the endothermic reaction,

$$H+O_2\rightarrow OH+H, \qquad (3)$$

at room temperature has small probability of occurring in the $\sim10^{-2}$ sec residence time in the reaction zone. In the experiments described we estimate that roughly 1 percent of the hydrogen atoms end up in HO_2 at the sampling orifice.

Experiments on the HO_2 problem are in progress and a complete report on this research will be presented later.

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[*] This research was supported by the Bureau of Ordnance, U. S. Navy.

[1] S. N. Foner and R. L. Hudson, J. Chem. Phys. 21, 1374 (1953).

Extra Laue Reflections of Tetraphenylethylene Crystal

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(Received June 25, 1953)

TETRAPHENYLETHYLENE was dissolved in alcohol which was heated till it dissolved completely, then benzene was added. The whole mixture was allowed to evaporate slowly; then the crystal of tetraphenylethylene was obtained. Morphological data indicates that it belongs to the holo axial monoclinic system with the axial ratio $a:b:c=1.213:1:1.078$, $\beta=68°20'$. The rotation photographs about the three crystallographic axes using Ni radiation show $a=11.36$ Aμ, $b=9.37$ Aμ, and $c=10.10$ Aμ. The density (ρ) was found to be 1.057. The number of molecules per unit cell was calculated to be one. A systematic study of x-ray reflections from a large number of planes, indicates that the space group of this crystal is P^2/m. The crystal was set with the needle axis (b-axis) vertical and x-ray (unfiltered Ni-radiation) falls normal to (001) face. Laue photographs were taken in this position at an interval of 5°.