

Observation of Excited States in Ozone near the Dissociation Limit

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Several calculations suggest that the lowest triplet states of ozone lie near the dissociation limit. Using electron energy-loss spectroscopy, we have observed a broad feature beginning at 1.3 eV, with a maximum at 1.65-eV energy loss. This structure is present only under large momentum-transfer conditions, indicative of the excitation of optically forbidden states. Together with the calculations, these data demonstrate that one or more excited states of ozone exist which are stable against dissociation.

The immediate importance attached to understanding ozone chemistry, coupled with recent experimental results¹⁻³ that hint of the possible existence of low-lying excited states, has led to both theoretical predictions^{4,5} of and experimental searches for these states. We report here the first observation of excited states near the dissociation limit. The optically allowed ozone transitions, as seen by electron-impact spectroscopy, have been presented previously.⁶

Pulsed radiolysis experiments¹ in O₂ have shown transient absorption which the authors attribute to vibrationally excited ozone. A subsequent experiment² verifies the existence of the absorption spectrum, but the authors suggest that the transient species has not been "unequivocally established as vibrationally excited ozone." Two large-scale configuration-interaction calculations^{4,5} predict respectively that the ³B₂ state and the ³B₂ (0.4 eV), ³A₂ (0.3 eV), ¹A₂ (0.1 eV), and ³B₁ (≈0 eV) states are bound with respect to the dissociation energy of 1.13 eV by the energies indicated in parentheses.

Electron scattering experiments can observe optically forbidden transitions by selective adjustment of the scattering parameters toward large momentum transfer. While small-angle scattering at high incident energies follows electric dipole selection rules, large-angle scattering at energies just above the threshold for the excitation enhances the excitation of forbidden states.^{7,8} Excitation of the three triplet states (³B₂, ³A₂, ³B₁) will proceed via exchange, while excitation of the ¹A₂ state occurs via electric quadrupole excitation. The use of near-threshold impact energies will favor the exchange interaction and thus the excitation of triplet states. We therefore expect that structure in the energy-loss spectrum, present only for low incident energies and large scattering angles, is due primarily to excitation of triplet states. We wish

to test whether there is such structure in ozone at or near the predicted⁵ values of energy loss and, in particular, whether the measured vertical excitation energies imply that the lowest state (at least) is stable against dissociation.

We have used an electron monochromator-analyzer combination designed by Kuyatt and co-workers⁹ to produce electron beams with energies of 4 to 8 eV with a resolution of about 90 meV (full width at half-maximum). These electrons are scattered from ozone confined in a gas cell at a pressure of approximately 2 Pa (15 mTorr) and are energy analyzed at scattering

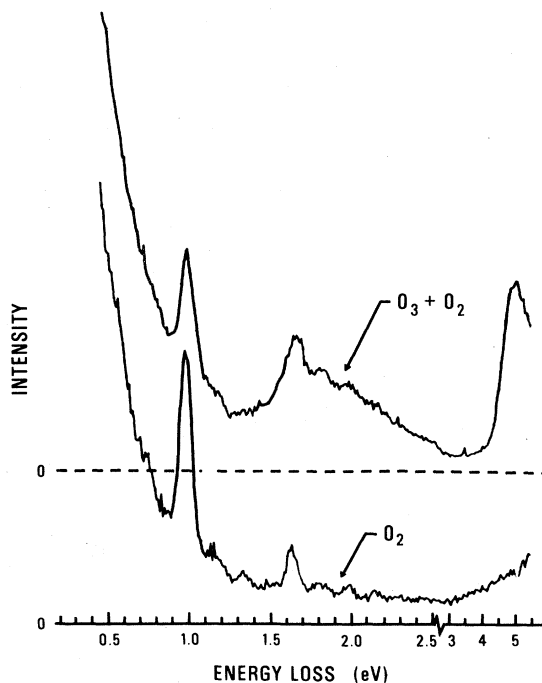


FIG. 1. Top: Energy-loss spectrum of ozone-oxygen mixture taken at 90° with a constant final energy of 5.5 eV. Bottom: Energy-loss spectrum of oxygen taken under the same conditions.

angles of 45° , 75° , or 90° . The analyzer is set to accept electrons of a fixed energy of a few electron volts independent of the incident energy. In this constant-final-energy (CFE) mode, the spectrum which results as the incident energy is swept is an energy-loss spectrum where each excitation is caused by electrons at a fixed energy above the threshold energy. The ozone is produced by an rf discharge in oxygen and is preferentially collected on cooled silica gel. The silica gel is subsequently warmed to release the ozone. We observed a sizable oxygen concentration in the ozone, requiring us to repeat each set of measurements using pure oxygen in order to subtract the oxygen background.

Figure 1 shows energy-loss spectra taken at a scattering angle of 90° and a constant final energy of 5.5 eV. The top curve is for ozone plus oxygen and the bottom one is for pure oxygen. An ozone concentration of approximately 50% was monitored at the source by optical absorption measurements using the mercury 253.7-nm line. The incident energy of the electrons was determined by adding a small amount of helium to the cell and observing the position of the $(1s2s^2)^2S$ resonance in elastic scattering. This was necessary because of the large change in contact potential observed in the apparatus when

ozone or pure oxygen are interchanged in the scattering cell. The pure oxygen curve shows the $a^1\Delta$ state (0.98 eV), the $b^1\Sigma$ state (1.63 eV), and a number of vibrational levels of the ground states. The top curve shows these features plus a broad peak between 1.3 and 2.4 eV. Both curves contain the tail of the elastic signal on the left, which becomes insignificant at about 1.2-eV energy loss.

Figure 2 shows the reduced energy-loss spectra for ozone taken at scattering angles of 45° , 75° , and 90° over the energy-loss range of 1.2 to 6 eV. The energies above threshold are 4.6, 6.2, and 3.1 eV, respectively. These curves were obtained by subtraction of the spectra due to pure oxygen taken under nearly identical conditions. Before subtraction, compensation was made for slight differences in the energy scale zero and resolution of pairs of spectra.¹⁰ The peaks at 4.9 eV (250 nm) are due to the Hartley band, the allowed transition responsible for much of the atmospheric ultraviolet attenuation. The broad feature beginning at 1.3 eV (950 nm) and peaked at about 1.65 eV (750 nm), seen only at low incident electron energies and large scattering angles, we ascribe to one or more optically forbidden excited states.

Some residual structure appears in these

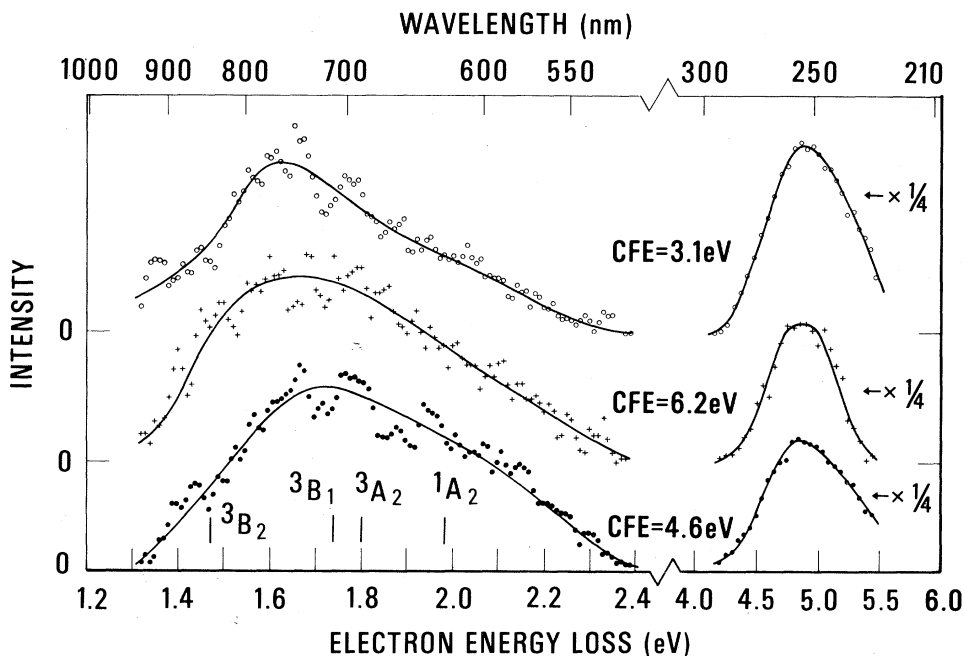


FIG. 2. Energy-loss spectra of ozone, at scattering angles of 45° (\square), 75° ($+$), and 90° (\circ). The three data sets are not plotted on the same intensity scale. The vertical lines at the bottom denote the calculated vertical excitation energies from Ref. 5.

curves because of the difficulty of exactly replicating, during the measurement of the pure oxygen data, the conditions under which the ozone data were taken. Slight differences in resolution and incident energy, and the variation of incident current with energy, cause some "leakage" of oxygen vibrational structure into the reduced curves. When all of our data sets are taken into consideration, this substructure can be seen to be an artifact.

These results can be compared with those of Hay, Dunning, and Goddard.⁵ Figure 2 shows their calculated vertical excitation energies to the 3B_2 , 3A_2 , 1A_2 , and 3B_1 states. The lowest excited state, the 3B_2 state, has a calculated adiabatic transition energy of 0.7 eV and a vertical transition energy of 1.47 eV. The difference between the calculated adiabatic and vertical energies is expected to be more accurate than either separately, with both subject to the same systematic offset. Since the dissociation energy is 1.13 eV, the 3B_2 state would be stable against dissociation if its vertical transition energy lies below 1.9 eV. The observed structure is approximately what would be expected from the sum of four broad peaks. In particular, even under the most extreme assumptions, given the shapes of the calculated energy surfaces, the intensity maximum near or below 1.7 eV shows that one or more of the states calculated are almost certainly stable against dissociation. This stability opens another channel in the normal three-body reaction for ozone formation, with the end product being a more highly reactive species of

ozone. This state will now require consideration in kinetics experiments and, depending on its lifetime, in atmospheric modeling as well.

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Measurement of the Zero-Field Hyperfine Structure of a Single Vibration-Rotation Level of Na₂ by a Laser-Fluorescence Molecular-Beam-Resonance Technique*

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By replacing the *A* and *B* magnets of the conventional molecular-beam-resonance technique with laser optical-pumping regions, we have developed a method for the observation of hfs in a single molecular-vibration-rotation level of arbitrary *J*. We obtain for the electric quadrupole and spin-rotation constants of the $X^1\Sigma_g^+$, $v''=0, J''=28$ level of Na₂: $eqQ = -463.7 \pm 0.9$ kHz; $|c| = 0.17 \pm 0.03$ kHz. We also report the first observation of a spin-rotation transition.

Much of our knowledge of the properties of free atoms and molecules has come from the molecular-beam-resonance technique developed principally by Ramsey and co-workers.¹ This method

is well suited to high-precision measurements of hyperfine structure in low rotational levels of neutral molecules. In an electric-deflection beam spectrometer, rotational levels of polar