Study of electronically excited states of ozone by electronenergyloss spectroscopy

Michael Allan, Nigel J. Mason, and Julia A. Davies

Additional information on J. Chem. Phys.

Study of electronically excited states of ozone by electron-energy-loss spectroscopy

Michael Allan
Institut de Chimie Physique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

Nigel J. Mason and Julia A. Davies
Department of Physics and Astronomy, University College London, London WC1E 6BT, England

Electronically excited states of ozone have been studied by electron-energy-loss spectroscopy. Two broad bands without visible vibrational structure are observed at 1.8 ± 0.2 eV and 2.05 ± 0.05 eV under scattering conditions favoring singlet excitation, that is a scattering angle of $\vartheta=10°$ and residual energy $E_r=20$ eV. The lower is assigned as $^1A_2$, the higher as $^1B_1$ (Chappuis band). Bands with rich vibrational structure are observed under scattering conditions favoring triplet excitation, $\vartheta=30°-135°$ and residual energy $E_r=1-3$ eV. At least two vibrational progressions can be discerned. The first has an origin at 1.30 eV, the origin of the second cannot be determined unambiguously, it is either at 1.53 or 1.45 eV. The well-known Hartley band and a number of other singlet and triplet excited states are observed at higher energy losses. Excitation functions and angular distributions of the triplet band at 1.30 eV and of the Hartley band are presented. The absolute value of the differential cross section for excitation of the Hartley band is given. © *1996 American Institute of Physics.* [S0021-9606(96)01838-7]

I. INTRODUCTION

Electronically excited states of ozone, in particular the low-lying states, are very interesting because of their environmental and technological relevance, but also from a purely scientific point of view—the small separation of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) of ozone results in an exceptional electronic structure. Many of the transitions are spin forbidden or have very low oscillator strengths, making electron-energy-loss spectroscopy (EELS)—with its relaxed selection rules—an interesting method of study. However to date only few electron-energy-loss studies of the electronic transitions of ozone have been reported probably because of the difficult preparation and handling of high purity ozone, and because of its corrosive nature. Pioneering work has been carried out by Celotta et al.[1] and Swanson and Celotta.[2] The energy-loss spectrum and absolute differential elastic cross sections were reported by Shyn and Sweeney.[3] Johnstone et al.[4] and Gingell et al.[5] reported differential oscillator strengths produced by EELS. Mason et al.[6] reported low-energy EELS using an electron trap.

In contrast, there is a substantial body of photoabsorption studies of ozone and only an incomplete account can be given here. A brief overview of earlier experimental and theoretical work has been given by Steinfeld, Adler-Golden, and Gallagher, et al.[7] Anderson and Mauersberger[8] recently reported a very high sensitivity absorption spectrum of the Wulf and the Chappuis bands in the 1–3 eV range. Recent synchrotron radiation spectra in the 3–11.3 eV range were given by Mason et al.[6] The most comprehensive information on the low-lying excited states, in particular triplets, stems from the laser-photoelectron spectra of the ozonide negative ion (anion photoelectron spectra, APES).[9]

In this paper we report EELS with improved resolution

and smaller statistical noise, revealing further details of the excited states. We also report the absolute differential cross sections (DCSs) for the excitation of one of the low-lying triplet states and of the Hartley band, both as a function of electron energy and of scattering angle.

II. INSTRUMENTATION

Preparation and handling of ozone of high purity requires considerable experience. We accomplished this task with the ozone production apparatus designed and constructed at the UCL. The techniques have been described previously by Johnstone et al.,[4] Davies et al.,[10] and Newson et al.[11]

The electron-energy-loss (EEL) spectrometer used to record the spectra has been described previously.[12,13] Ozone was introduced into the collision region from a storage bulb as an effusive beam through a nozzle with 250 μm diam and 0.3 mm long, kept at 45 °C. The spectra were, except where otherwise noted, corrected for the instrumental response function, determined on the elastic signal and near threshold ionization continuum of helium. Absolute differential cross sections (DCSs) were determined using the relative flow technique. The application of this technique was complicated by the decomposition of ozone in the metallic part of the gas handling system, including the capacitance manometer used to measure gas flow, and by the limited purity of ozone (although up to 97% ozone in the collision region was achieved[14]). The details of the procedure which we used to circumvent these problems have already been described.[14] These complications increase the uncertainty of the absolute values, accurate within ±40% (the uncertainty is larger for residual energies below about 0.2 eV). The energy-loss scale was calibrated on the elastic peak and is accurate within ±10 meV at energy losses below 3 eV, and within ±20 meV
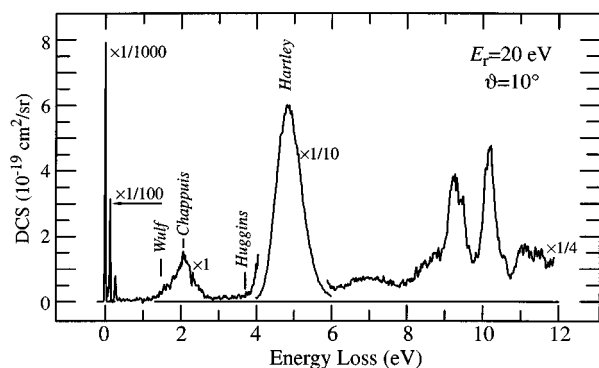
FIG. 1. Electron-energy-loss spectrum of ozone, recorded with a residual energy E_r of 20 eV and a scattering angle of 10°. Singlet state excitations are enhanced under these conditions. Weak signals due to oxygen and nitrogen have been subtracted from the spectrum. Portions of the spectrum are shown attenuated by the factors shown.

FIG. 3. Raw energy-loss spectrum of a typical ozone–oxygen mixture (top), and of pure oxygen (bottom), recorded under identical conditions. (The spectra are not on the same vertical scale.)

above 3 eV. The incident and residual energy scales were calibrated on the 19.366 eV resonance in helium and on sharp features in the vibrationally inelastic cross sections of O_2 in O_2/O_3 mixtures, and are accurate within ±20 meV. The resolution was between 20 and 25 meV (full width at half-maximum, in energy-loss mode). A Wien filter was used in the analyzer to prevent fragment anions from reaching the detector.

III. RESULTS AND DISCUSSION

A. Energy-loss spectra

Figures 1–4 show spectra with a wide range of energy losses, recorded with three representative combinations of residual electron energies and scattering angles. Triplet states are expected to be nearly absent with the relatively high residual energy and the nearly forward scattering angle used to record the spectrum in Fig. 1. On the other hand the scattering angle is sufficiently different from zero, making the momentum transfer sufficiently large to permit excitation not only by the electric dipole but also by higher multipoles. The energy-loss spectrum in Fig. 1 may thus be expected to re-
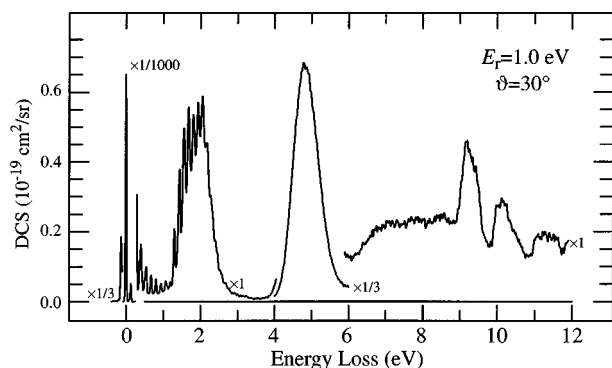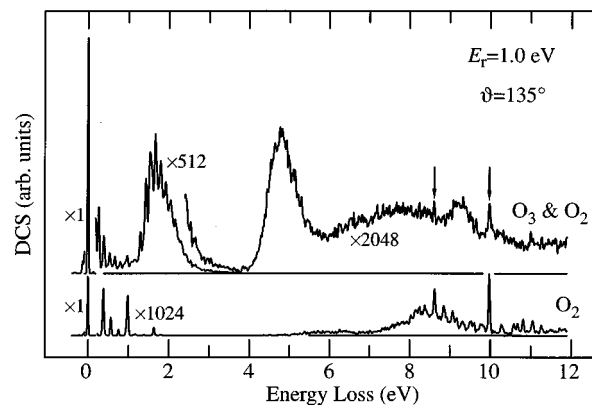
semble the light absorption spectrum, but with the dipole-forbidden singlet–singlet transitions slightly enhanced. The Wulf and the Chappuis bands are seen clearly in Fig. 1, but their intensity is very low: even the more intense Chappuis band is about 5000× weaker than the elastic peak. The position of the Huggins band is marked in Fig. 1, but the band is too weak to be discerned in the present spectrum. The rest of the spectrum resembles closely the absorption spectrum of Mason et al.[6]

Figure 2 shows an energy-loss spectrum recorded at a much lower residual energy, where resonant excitation of triplet states may be expected. The prominent vibrational progression in the 1.3–2.5 eV range must therefore be due to triplet states. A long progression of the symmetric stretch vibration of the electronic ground state is weakly excited in the 0–1.2 eV range. The resonance responsible for this excitation must be around 1.5 eV, and could be the same core excited resonance as the one causing dissociative attachment around 1.3 eV.[6,14] Comparison with Fig. 1 reveals additional diffuse bands in the 6–9 eV range which must also be due to triplet states.

FIG. 2. Energy-loss spectrum of ozone, recorded with low residual energy $E_r = 1.0$ eV and a moderate scattering angle $\vartheta = 30°$. Triplet state excitations are enhanced under these conditions. Weak signals due to oxygen and nitrogen have been subtracted from the spectrum.
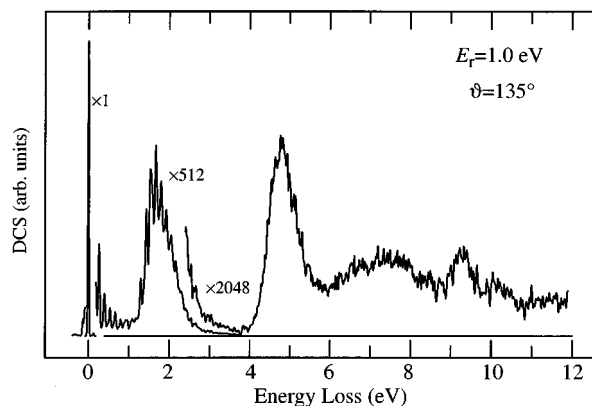

FIG. 4. Energy-loss spectrum of ozone recorded with low residual energy and a large scattering angle. Signals due to oxygen and nitrogen have been subtracted.
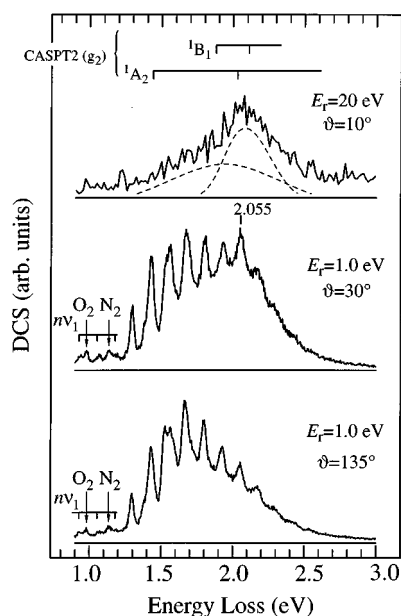
FIG. 5. Energy-loss spectra of the low-lying electronically excited states. Impurity oxygen and nitrogen signals were not subtracted from these spectra, and are indicated by arrows. High vibrational levels of the electronic ground state are also marked on the left-hand side. The calculated singlet excitation energies of Ref. 15 are shown above the top spectrum. The calculated adiabatic and the vertical excitation energies T_0 and T_v are indicated by short vertical lines, which are connected by a horizontal line whose length gives an indication of the bandwidth.
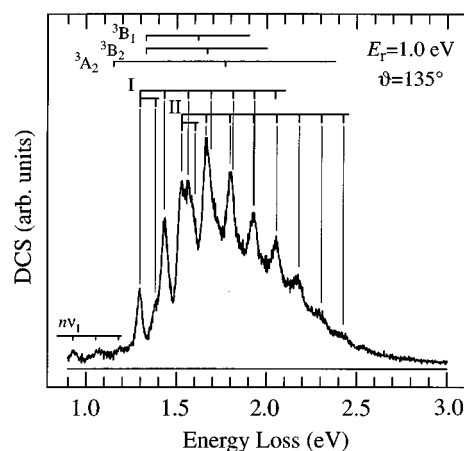

FIG. 6. Energy-loss spectrum of the low-lying triplet states, with oxygen and nitrogen signal subtracted. The calculated triplet excitation energies of Ref. 16 are shown above the top spectrum in the same format as in Fig. 5.

A point requiring careful consideration is the contribution of the oxygen impurity to the ozone spectra. A oxygen content as low as 3% was reached in the present experiments,[14] but it was not constant and increased slowly during the acquisition. The coefficients used in the subtraction of the oxygen signal were therefore determined on the sharp oxygen peaks at 8.66 and 9.98 eV which can easily be discerned in the spectrum of the mixture. Figure 3 illustrates a typical raw ozone spectrum and a spectrum of pure oxygen recorded under the same scattering conditions. The nitrogen signal in the energy-loss range of vibrational excitation had to be subtracted as well since, although the fraction of nitrogen in the sample gas was small, the $^2\Pi_g$ resonance causes a very large cross section for vibrational excitation at low residual energies (1–3 eV). The result of subtracting the oxygen and nitrogen signals from the raw spectrum in Fig. 3 is shown in Fig. 4. It has been recorded with the same low residual energy as the spectrum in Fig. 2, but at a large scattering angle $\vartheta = 135°$. The major differences are in the shape of the 1.3–2.5 eV band and the appearance of the spectrum in the 6–12 eV range.

Figure 5 shows the region of the low-lying electronically excited states in detail. The top spectrum, recorded under "singlet excitation" conditions, can be interpreted as a superposition of two roughly Gaussian bands, indicated in the figure by dashed lines. Both the energies and widths of the two bands agree well with the theoretical predictions of Borowski et al.[15] for the $^1A_2$ and the $^1B_1$ states (indicated in Fig. 5) and we therefore choose this assignment.

The two energy-loss bands resemble the Wulf and Chappuis bands of photoabsorption spectra in terms of transition energies, but not in terms of relative intensities. The height of the lower-lying $^1A_2$ band is about one-half the height of the higher-lying $^1B_1$ band in the present spectra, whereas the ratio is about 1:10 in the absorption spectrum given by Anderson and Mauersberger.[8] The absorption spectrum exhibits a pronounced vibrational structure at energies below 1.6 eV, which does not appear in the present energy-loss spectrum, although the large statistical noise of the present spectrum precludes a definitive statement. The Chappuis band in the absorption spectrum has been assigned to the $^1B_1$ state.[8] The assignment of the Wulf band in the absorption spectrum is not fully established. An assignment to the $^1A_2$ state has often been proposed,[7] the transition from the ground state being vibronically allowed with simultaneous excitation of the asymmetric stretch vibration, but an assignment to the triplet counterpart $^3A_2$ was recently proposed by Anderson and Mauersberger[8] and this proposition was supported by theory.[16] It thus appears that the lower of the two singlet bands in the top spectrum of Fig. 5 (whose assignment to a triplet is precluded by the scattering conditions under which it is observed) is not simply the Wulf band, but is the $^1A_2$ state, the excitation of this dipole forbidden transition being enhanced by higher multipoles in the energy-loss spectrum. It must be emphasized, however, that this assignment of the energy-loss band does not contradict the assignment of the Wulf band in the optical spectrum to the $^3A_2$ state.

Triplet bands with well-developed vibrational structure appear on the spectra recorded at higher scattering angles and low residual energy. The spectrum in the center of Fig. 5 appears to be intermediate between the top and the bottom spectra. It appears that the $^1A_1$ state Chappuis band contributes signal to the spectrum at 30° and $E_r = 1$ eV, and that this contribution diminishes at 135°. The low-lying triplet states are shown in detail in Fig. 6 and compared with the adiabatic and vertical excitation energies calculated by Borowski

et al.[15] Similar adiabatic and vertical excitation energies were also calculated by Tsuneda, Nakano, and Hirao.[17] The comparison with theory suggests that the observed vibronic peaks are due to the $^3B_2$ and $^3B_1$ states. However, the relative ordering of the two states cannot be decided on the basis of the present spectra alone; both the present experiment and the results of the two calculations indicate that the two states nearly coincide in energy. The third peak, at around 1.55 eV, is a doublet and indicates clearly that more than one electronic state is responsible for the vibrational peaks in the 1.3–2 eV range. Figure 6 shows what appears to be the most plausible explanation of the observed peaks in terms of two progressions, labeled I and II. Progression I has an origin at 1.297 ± 0.02 eV, in excellent agreement with the value of 1.29 ± 0.03 eV observed in absorption and assigned to the $^3B_2$ state by Anderson and Mauersberger[8] and with the value of 1.30 eV obtained from anion photoelectron spectra (with the same assignment) by Arnold et al.[9] The origin of progression II, as indicated in Fig. 6, is at 1.527 ± 0.02 eV. This value is less certain; however, it cannot be excluded that the origin lies one bending vibration lower, at 1.43 eV, in which case it would overlap with the second member of progression I. The latter value would be in better agreement with the values given as the origin of the $^3B_1$ state by Anderson[8] (1.48 ± 0.03 eV) and by Arnold[9] (1.45 eV).

It is interesting to compare the band shapes of the triplet states as they appear in the present energy-loss experiment, where the transitions proceed from the ground state of neutral ozone, with the laser detachment experiment of Arnold, where the initial state is the ground state of the ozone anion. The striking difference is the larger Franck–Condon width in the present experiment, indicating that the geometry of the low lying electronic states is closer to the geometry of the anion ground state than to the geometry of neutral ozone. The present spectra are dominated by a stretching vibration (almost certainly ν_1), whereas the anion photoelectron spectra are dominated by the bending vibration. This observation is in nice agreement with the calculated geometries of the excited states,[15,17] indicating substantially different bond lengths for the ground and the excited states, and very similar bond lengths (but in some cases substantially different bond angles) for the anion and the excited states.

Arnold et al.[9] report a band at 1.58 eV and assign it to the $^1A_2$ state. A band is observed at this energy in the present spectra, but it fits the third member of progression I, so that the present spectra do not provide sufficient information to postulate a separate electronic state at 1.58 eV. The $^1A_2$ state is, furthermore, already assigned to the diffuse band in the top spectrum of Fig. 5. The spectra from the two experiments cannot be compared directly, however, because the $^1A_2$ band is expected to have a substantially different shape, in particular to be much narrower, in the laser APES experiment of Arnold et al.[9] No band was observed at 1.58 eV by Anderson and Mauersberger[8] in their photoabsorption spectra, and this fact has been interpreted as a confirmation of the assignment of Arnold et al., since the transition to the $^1A_2$ state is forbidden in photoabsorption (without a simultaneous excitation of ν_3).
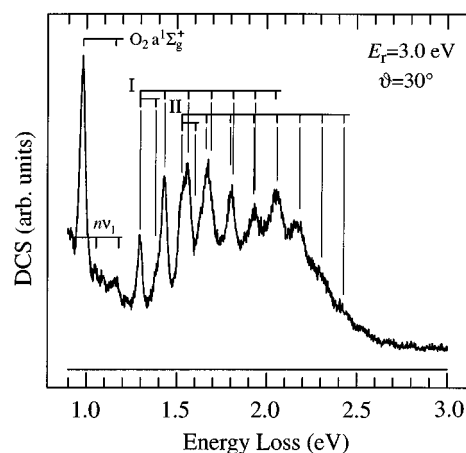

FIG. 7. Energy-loss spectrum of the low-lying triplet states, recorded with a higher residual energy. The oxygen content of the sample was much higher than in the other spectra of this work and was not subtracted.

Overlapping bands can often be distinguished in electron-energy-loss spectroscopy by recording spectra under different scattering conditions, taking advantage of the different dependence of the DCSs for their excitation on scattering angle and electron energy. The singlet and the triplet states can clearly be distinguished in this way, as shown in Fig. 5. However varying the scattering angle does not help in distinguishing the various triplet states since the relative intensities of the individual vibronic peaks changed little between 30° and 135°. We attempted to gain more insight by recording a spectrum at a different electron energy, as shown Fig. 7. The quasicontinuous background at low energy loss is caused by the excitation of high vibrational levels of the ground electronic state of ozone by the $^2A_1$ shape resonance at 4.2 eV.[14] The relative intensities of the individual vibronic peaks changed little between the residual energy of 1 eV (Fig. 5) and 3 eV (Fig. 7). The DCSs for exciting the various triplet states therefore appear to depend on the incident energy in a very similar way and do not bring clarity into the overlapping triplet transitions in the 1.2–2.5 eV range.

One final observation can be made when the two spectra recorded at $\vartheta = 30°$ (in Figs. 5 and 7) are compared to the $\vartheta = 135°$ spectrum in Fig. 6: The vibronic peak at 2.055 eV is enhanced in intensity in the 30° spectra, even when the variations of the intensity of the underlying background are disregarded, indicating that this peak is not only a member of progressions I and II, but that there is another underlying transition at this energy. This finding is in agreement with the observation of a band at 2.057 eV by Arnold et al.[9] and with the observation of a weak vibrational structure on the Chappuis band, with the first and strongest peak at 2.058 eV.[8] In both cases the 2.058 eV band is assigned to the $^1B_1$ state, and this assignment is not contradicted by the present observations. It is somewhat puzzling, however, since the vibrational structure of the $^1B_1$ state is not observed at low scattering angle and high residual energy in the top spectrum of Fig. 5.
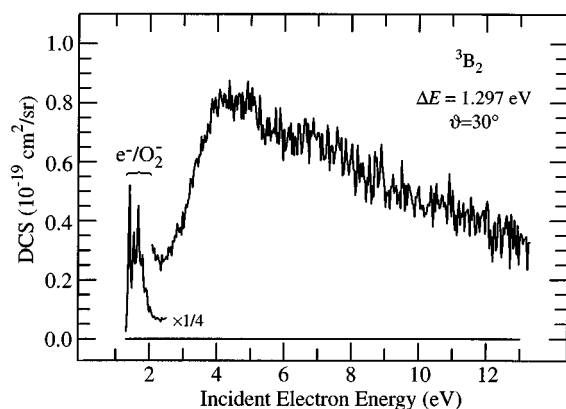
FIG. 8. Differential cross section for exciting the vibronic level at 1.30 eV as a function of the incident electron energy. The structured signal just above threshold is not due to electronic excitation, but to electrons detached by vibrationally excited O_2^- (Ref. 18).
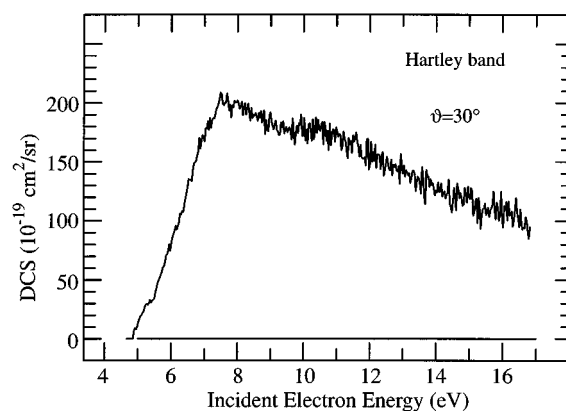

FIG. 10. Differential cross section for exciting the Hartley band as a function of the incident electron energy. The absolute values refer to the sum of all rovibronic transitions.

B. Excitation cross sections

Figure 8 shows the DCS for exciting the vibronic level at 1.3 eV as a function of the incident electron energy. (The structured signal near threshold is caused by autodetaching O_2^-, formed by dissociation of ozone.[18]) The curve is characteristic for the excitation of a triplet state; it has a broad maximum about 2.5 eV above threshold, probably caused by a broad core excited shape resonance, and is followed by a gradual decrease. Figure 9 shows the angular distribution of exciting the same electronic state, but the $v=1$ level was taken to gain intensity. The angular distribution is not symmetric around 90° and thus cannot be interpreted simply in terms of a single partial wave.

Figure 10 shows the excitation function of the Hartley band. The curve was recorded by scanning the incident and residual energies with the energy-loss fixed at $\Delta E = 4.84$ eV (band maximum) and correcting the resulting curve for the instrumental response curve. In order to facilitate future comparisons with theory the absolute values given in Fig. 10 are normalized to refer to the sum of all rovibronic transitions of the Hartley band. This was achieved by recording an energy-loss spectrum at one fixed scattering angle, integrat-

ing under the entire Hartley band, and using the resulting value to normalize the excitation function in Fig. 10 (the procedure was described in more detail previously[19,20]). Figure 11 shows the angular distribution of electrons having excited the Hartley band. It was obtained by scanning the scattering angle with the energy-loss fixed at $\Delta E = 4.84$ eV, correcting for the instrumental response curve, and normalizing the absolute values to reflect the sum of all rovibronic transitions of the Hartley band as above. The angular distribution is forward-peaked, characteristic of a singlet transition.

After completing this manuscript we learned about a very recent measurement of the absolute DCSs for the excitation of the Hartley band by Sweeney and Shyn.[21] Their results cannot be compared with the present data directly because measurements were not carried out at exactly the same energies and scattering angles, but comparisons at similar scattering conditions can be made. It indicates good agreement in terms of the trends observed: The angular distribution of the DCS at 7–10 eV has a peak in the forward direction, decreases with increasing scattering angle until $\vartheta \approx 40°$, but a plateau is observed at higher scattering angles (Fig. 11). The present absolute values are generally some-
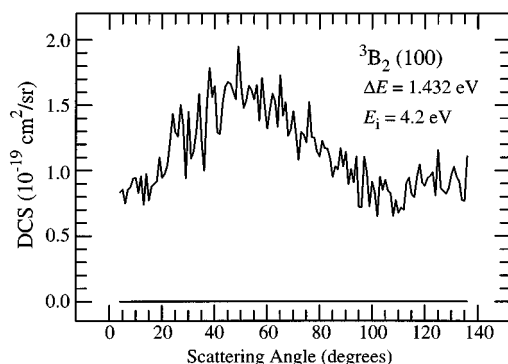

FIG. 9. Differential cross section for exciting the vibronic level at 1.43 eV as a function of the scattering angle.
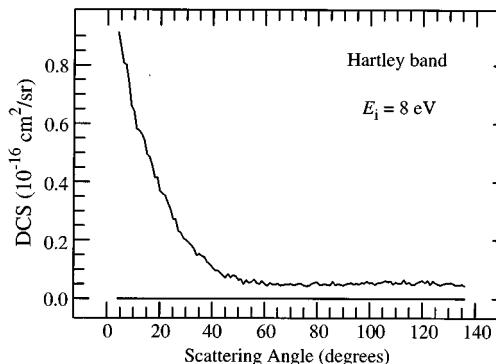

FIG. 11. Differential cross section for exciting the Hartley band as a function of the scattering angle.

TABLE I. Differential cross sections for exciting the Hartley band by electron impact. The cross sections refer to the sum of all vibronic transitions and are given in units of 10^{-18} cm^2/sr. The uncertainty is $\pm 26\%$ for the DCS of Ref. 21, $\pm 40\%$ for the present work.

ϑ (deg)	4	12	36	60	84	108	132
7 eV[a]		26	12	6.7	3.8	2.9	1.8
10 eV[a]		78	9.9	4.5	4.4	4.3	3.7
8 eV[b]	85	54	14	5.8	5.9	8.2	7.4

[a]Reference 21.
[b]Present study.

what higher, but the two measurements generally agree within the combined error limits, as indicated in Table I.

IV. CONCLUSIONS

An asymmetric energy-loss band can be observed under scattering conditions where singlet excitation dominates. It is continuous, although weak vibrational structure may escape observation because of the relatively high level of statistical noise. The band can be plausibly interpreted as resulting from overlap of a broader band peaking at 1.8 ± 0.2 eV and a narrower band peaking at 2.05 ± 0.07 eV. The bands can be assigned as $^1A_2$ and $^1B_1$ by comparison with theoretical predictions,[15] resulting in very good agreement both in terms of transition energies and bandwidths.

Many vibronic transitions are observed under scattering conditions where triplet excitation dominates. The majority of the vibrational peaks can be plausibly, although not unambiguously, divided into two progressions, labeled I and II in Fig. 6. The first progression starts at 1.297 ± 0.01 eV, in excellent agreement with the value of 1.30 eV of Arnold et al.[9] and the value of 1.29 ± 0.03 eV of Anderson and Mauersberger.[8] An obvious choice of the origin of the second progression is 1.528 ± 0.01 eV, but an alternative origin at around 1.45 eV, one bending vibration lower, is also possible. The later is in a better agreement with the value of 1.45 eV given both by Arnold et al.[9] and by Anderson and Mauersberger[8] (and assigned as $^3B_1$). Vibrational excitation is dominated by the stretch vibration ν_1 (0.135 ± 0.01 eV for both progressions), as expected from the substantial difference of the calculated O–O distances in the ground and the excited states. Weaker excitation of the bending vibration ν_2 can also be discerned. We point out that the two progressions proposed in Fig. 6 explain the important features, but not necessarily all fine details of the observed spectrum. In particular it is not quite clear why the doublet at 1.528/1.562 eV is broader than any of the remaining vibronic features. This observation could be interpreted as an indication that the vibrational structure is irregular and can be explained in detail only when vibronic interaction and the intersection of the triplet state potential surfaces, in particular of the $^3A_2$ and $^3B_1$ states, analogous to the vibronic interaction of the corresponding singlet states,[22–24] are taken into account. The same conclusion has been reached by Anderson and Mauersberger on account of irregularities in the isotope shifts.[8]

Intensity variations permit the conclusion that there is an additional vibronic peak at 2.055 ± 0.03 eV not belonging to the above two progressions. The energy of this peak agrees well with the first and most pronounced vibrational structure of the Chappuis band in photoabsorption[8] and with the observation of a band at 1.58 eV by Arnold et al.[9] The peak was assigned to the $^1B_1$ state in both cases. It remains somewhat puzzling, however, why this vibronic band is observed with low residual energies in the present experiment, whereas the same $^1B_1$ state appears structureless at low scattering angles and high residual energy. An explanation could be sought in an assumption that different vibrational levels of the same electronic state are excited with different preference under different scattering conditions. It could be that, paradoxically, the triplet states are more pronounced in the photoabsorption spectra, where they appear because of spin-orbit coupling[16] (and, of course, in the energy-loss spectra at low residual energy and large scattering angle) than in the low scattering angle, 20 eV residual energy spectrum, because the dipole forbidden $^1A_2$ state and the $^1B_1$ state with its extremely small oscillator strength, are excited more efficiently by higher multipoles in electron impact than in photoabsorption.

The lowest triplet state, observed by Arnold et al.[9] at 1.18 eV and by Anderson and Mauersberger[8] at 1.185 ± 0.002 eV and assigned as $^3A_2$, cannot be discerned in the present spectra. Its observation in EELS is hindered by the excitation of high vibrational levels of the electronic ground state, but despite this the lack of observation reveals the somewhat puzzling fact that the cross section for exciting the $^3A_2$ state is at least a factor of 10 smaller than the cross section for the higher triplet states.

We conclude by pointing out that the main spectroscopic features of the five low-lying excited states appear established, but a number of details remain puzzling. Further insight would be gained if the band shapes could be calculated taking into account the vibronic interactions and the intersections of the potential surfaces, and then comparing the results with the present spectra. Calculations of the excitation cross sections for the low lying triplet states would also be very interesting, in particular if they are able to reproduce the anomalously low cross section for exciting the $^3A_2$ state.

[1] R. J. Celotta, S. R. Mielczarek, and C. E. Kuyatt, Chem. Phys. Lett. **24**, 428 (1974).

[2] S. N. Swanson and R. J. Celotta, Phys. Rev. Lett. **35**, 783 (1975).

[3] T. W. Shyn and C. J. Sweeney, Phys. Rev. A **47**, 2919 (1993).

[4] W. M. Johnstone, N. J. Mason, W. R. Newell, P. Biggs, G. Marston, and R. P. Wayne, J. Phys. B **25**, 3873 (1992).

[5] J. M. Gingell, J. A. Davies, and N. J. Mason, Physicalia **17**, 113 (1995).

[6] N. J. Mason, J. M. Gingell, J. A. Davies, H. Zhao, I. C. Walker, and M. Siggel, J. Phys. B (in press).

[7] J. I. Steinfeld, S. M. Adler-Golden, and J. W. Gallagher, J. Phys. Chem. Ref. Data **16**, 911 (1987).

[8] S. M. Anderson and K. Mauersberger, J. Geophys. Res. **100**, 3033 (1994).

[9] D. W. Arnold, C. Xu, E. H. Kim, and D. M. Neumark, J. Chem. Phys. **101**, 912 (1994).

[10] J. A. Davies, W. M. Johnstone, N. J. Mason, P. Biggs, and R. P. Wayne, J. Phys. B **26**, L767 (1993).

[11] K. A. Newson, S. M. Luc, S. D. Price, and N. J. Mason, Int. J. Mass Spectrosc. Ion Proc. **148**, 203 (1995).

[12] M. Allan, J. Phys. B **25**, 1559 (1992).

[13] M. Allan, J. Phys. B **28**, 5163 (1995).

[14] M. Allan, K. R. Asmis, D. B. Popovic, M. Stepanovic, N. J. Mason, and J. A. Davies, J. Phys. B **29** (in press).

[15] P. Borowski, M. Fülscher, P.-A. Malmqvist, and B. O. Roos, Chem. Phys. Lett. **237**, 195 (1995).

[16] M. Braunstein, R. L. Martin, and P. J. Hay, J. Chem. Phys. **102**, 3662 (1995); B. Minaev and H. Agren, Chem. Phys. Lett. **217**, 531 (1994).

[17] T. Tsuneda, H. Nakano, and K. Hirao, J. Chem. Phys. **103**, 6520 (1995).

[18] M. Allan, K. R. Asmis, D. B. Popovic, M. Stepanovic, N. J. Mason, and J. A. Davies, J. Phys. B (in press).

[19] M. Allan, J. Chem. Phys. **101**, 844 (1994).

[20] M. Allan, J. Phys. B **28**, 4329 (1995).

[21] C. J. Sweeney and T. W. Shyn, Phys. Rev. A **53**, 1576 (1996).

[22] W. Domcke, C. Woywod, and M. Stengle, Chem. Phys. Lett. **226**, 257 (1994).

[23] A. Banichevich and S. D. Peyerimhoff, J. Chem. Phys. **96**, 6580 (1992).

[24] M. Braunstein and R. T Pack, J. Chem. Phys. **96**, 6378 (1992).