

Electron impact excitation of carbon monoxide in comet Hale-Bopp

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Received 12 November 2008; revised 15 December 2008; accepted 2 January 2009; published 3 February 2009.

[1] The fourth positive emissions of carbon monoxide in the coma of comet Hale-Bopp have been assumed to be due mainly to fluorescence induced by sunlight. Based on this assumption they were used to deduce the abundance of carbon monoxide in the comet, giving a value higher than in other comets. Emissions produced by electron impact excitation of CO were not considered. Recent measurements and theoretical calculations of integral cross sections for electron impact excitation of CO allow the contribution of electron impact to be calculated, giving about 40% of the total. This implies that the abundance of CO in the outer coma of comet Hale-Bopp was only 60% of that previously deduced. However, as the high proportion of CO in comet Hale-Bopp was also seen in some other measurements, alternative explanations are considered. The method of calculation is tested by successfully predicting the O I emission at 1356 Å, supporting the belief that this line is due to electron impact excitation. **Citation:** Campbell, L., and M. J. Brunger (2009), Electron impact excitation of carbon monoxide in comet Hale-Bopp, *Geophys. Res. Lett.*, 36, L03101, doi:10.1029/2008GL036641.

1. Introduction

[2] Solar heating causes the emission of gases (principally water, carbon monoxide and carbon dioxide) from comet nuclei. Sunlight acting on the gases produces photodissociation and photoionisation, leading to a large number of chemical species, ions and photoelectrons. Radiative emissions from the gases are produced by solar induced fluorescence, prompt emission from excited species produced in dissociation, and radiative decay following photoelectron excitation. The latter is regarded as a minor process [Feldman, 2006] except for a few transitions which cannot be produced by photoexcitation. For example, in a UV spectrum of comet Hale-Bopp, an O I line at 1356 Å was identified as being due to electron impact excitation while the fourth positive ($A^1\Pi \rightarrow X^1\Sigma^+$) bands of CO were assumed to be due to solar fluorescence. In calculations based on this assumption, it was found that the proportion of CO to H₂O in comet Hale-Bopp is much higher than the average in comets (30% rather than 15%) and reaches a higher proportion (40%) at some distance from the comet [McPhate *et al.*, 1999]. This high proportion was supported by infrared measurements by Brooke *et al.* [2003] which gave 37%. However, DiSanti *et al.* [2001] deduced a smaller proportion of 24%.

[3] Recent experimental and theoretical determinations of integral cross sections for electron impact excitation of vibrational levels 0–7 of the $A^1\Pi$ state of CO allow calculation of the expected emissions due to electron impact. The 1356-Å emission is calculated and found to be within 17% of the observation above, supporting the identification of this line as being due to electron impact. The photoelectron spectrum is scaled to give the best fit to this line and applied to make predictions of emissions from CO($A^1\Pi$). The results of the earlier calculations for fluorescence only are reproduced to verify the methods of calculation. The contribution of electron impact is then included and is found to be about 65% of that due to fluorescence. This implies that the proportion of CO in comet Hale-Bopp is about 60% of that previously calculated, and so in agreement with the lower value measured by DiSanti *et al.* [2001].

[4] The electron impact contribution was determined in two different calculations. First the total brightness of selected CO lines was calculated, for comparison with a value determined by McPhate *et al.* [1999]. This does not require fitting to the experimental CO data and provides the main result, that electron impact excitation gives ~40% of the total emissions. A more complete calculation, including fitting to the measurements, verified the fitting performed by McPhate *et al.* [1999] and predicted the same 40% contribution from electron impact. However, if the fit to the measurements is applied only to lines at longer wavelengths, the predicted emissions are much larger. This would give an unreasonably large CO abundance if only fluorescence is considered, but gives a value similar to that determined by McPhate *et al.* [1999] when electron impact is considered.

2. Calculation Methods and Input Data

[5] Emissions produced by electron impact excitation can be calculated using “statistical equilibrium” [Cartwright, 1978]. The electron flux spectrum (i.e., the number of electrons crossing a unit area in unit time, as a function of electron energy) is multiplied by the electron impact excitation cross sections to determine the excitation rate. Radiative transitions from higher levels are added to this to give the gain. The deexcitation rate is the sum of the radiative transition rates to lower levels and quenching rates in collisions with other species. Assuming that the gain and loss rates are the same, the populations of the excited states and hence the radiative transition rates can be calculated. Initially the populations are not known, but are determined by repetitive solution of the continuity equations for all levels until stable values are achieved. The volume emission rate (photons cm⁻³s⁻¹) for each radiative transition is then given as the population of the upper level multiplied by the transition probability.

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Table 1. Transition Probabilities A (s^{-1}) for O I Transitions^a

Wavelength (Å)	A (s^{-1})	Transition
1 355.598	4.20×10^3	$3s^5S^{\circ} \rightarrow 2p^4\ ^3P(0)$
1 358.512	1.36×10^3	$3s^5S^{\circ} \rightarrow 2p^4\ ^3P(1)$
1 727.106	5.32×10^{-3}	$3s^5S^{\circ} \rightarrow ^1D$
3 947.586	4.87×10^5	$4p^5P \rightarrow 3s^5S^{\circ}$
6 726.537	6.44×10^2	$3p^3P \rightarrow 3s^5S^{\circ}$
7 775.388	3.69×10^7	$3p^5P \rightarrow 3s^5S^{\circ}$

^a[Ralchenko *et al.*, 2008].

[6] Cross sections for electron impact excitation of levels 0–7 of the $A^1\Pi$ excited state of CO are taken from recent “BE f -scaled” theoretical values that are consistent with recent measurements [Kato *et al.*, 2007]. Transition probabilities for CO were determined by combining branching ratios deduced from Table 2 of Tozzi *et al.* [1998] with lifetimes from Eidelsberg and Rostas [1992].

[7] To predict the O I emissions around 1356 Å required calculation of the transitions between the states and levels listed in Table 1. The transition probabilities are from the NIST data base [Ralchenko *et al.*, 2008]. The electron impact excitation cross sections, for excitation from the ground state $O(2p^4\ ^3P)$, are from Laher and Gilmore [1990] for $O(4p^5P)$, while those for $O(3s^5S^{\circ})$, $O(3p^3P)$ and $O(3p^5P)$ are averages of calculated values by Zatsarinny and Tayal [2002] and Barklem (P. S. Barklem, Electron-impact excitation of neutral oxygen, 2006, <http://arxiv.org/abs/astro-ph/0609684v1>).

[8] As the lifetimes of the O I and CO excited states are very short, it is not expected that collisional quenching is significant [McPhate *et al.*, 1999] but quenching was included to be sure. To calculate quenching rates, a density of 10^4 cm^{-3} for H_2O was taken from a previous model [Lovell *et al.*, 2004], then densities of CO and O atoms were set at 10^3 cm^{-3} and 10^2 cm^{-3} , based on ratios (to H_2O) calculated by Bhardwaj *et al.* [1990]. Quenching rates for excited CO and O I are not known to us, so as the point of the calculation was to show that quenching is insignificant, an improbably large value of $10^{-9}\text{ cm}^3\text{ s}^{-1}$ was used. It was verified that there was no significant difference when quenching was included.

[9] The photoelectron flux spectrum was obtained from a calculation by Bhardwaj *et al.* [1990], at solar minimum. Of the two spectra available, the one further from the comet was used. As the electron density for this flux spectrum is $26.2\text{ electrons cm}^{-3}$ and a density of $200\text{ electrons cm}^{-3}$ was calculated at a distance of 160000 km from Hale-Bopp [Lovell *et al.*, 2004], the photoelectron spectrum of Bhardwaj *et al.* [1990] was multiplied by 7.63 for the present calculation.

3. Calculation of O I Emissions

[10] To test our concepts and methods of calculation, a prediction was made of the O I emissions around 1356 Å in the measured spectrum of McPhate *et al.* [1999, Figure 3 (bottom)]. The predictions of the emissions due to electron excitation at 1356 Å and 1358 Å are shown in Figure 1, along with the measurements. The shape of the fitted peaks is a combination of a Gaussian profile with standard deviation $\sigma = 1.43\text{ Å}$ (explained later) and an averaging

with a 3-Å wide rectangular function to emulate the 5-pixel averaging applied to the raw data by McPhate *et al.* [1999].

[11] Given the errors involved (such as 100% for the electron density [Lovell *et al.*, 2004]), the good agreement of the calculated O I contribution (the sum of the two lines) with the measurement at 1356 Å may be fortuitous. However, it is consistent with the belief [McPhate *et al.*, 1999] that the 1356-Å line is due to electron impact, and shows that our methods of calculation are credible.

[12] The calculated sum is scaled to the measurements to give an equal area for the wavelength range where the calculated value exceeds half of its maximum. The resultant scaling factor of 1.17 is applied to the calculated CO emissions. This neglects contributions from other mechanisms, such as dissociative excitation, charge exchange or chemical reactions, to the O I $3s^5S^{\circ}$ state.

4. Total Brightness Calculation

[13] McPhate *et al.* [1999] chose a subset of the CO emission bands that were relatively faint (implying optically thin) and not blended with emissions from other species. For the selected lines they measured a total brightness of $230 \pm 30\text{ R}$, from which they calculated a column density for CO of $(4.0 \pm 0.5) \times 10^{14}\text{ molecules cm}^{-2}$, based on the assumption that all the emission is produced by fluorescence. The calculation used

$$\bar{N} = 10^6 \frac{B}{g} \quad (1)$$

to determine the column density \bar{N} (cm^{-2}) from the observed brightness B in Rayleighs (R) and a “ g -factor” tabulated by Tozzi *et al.* [1998].

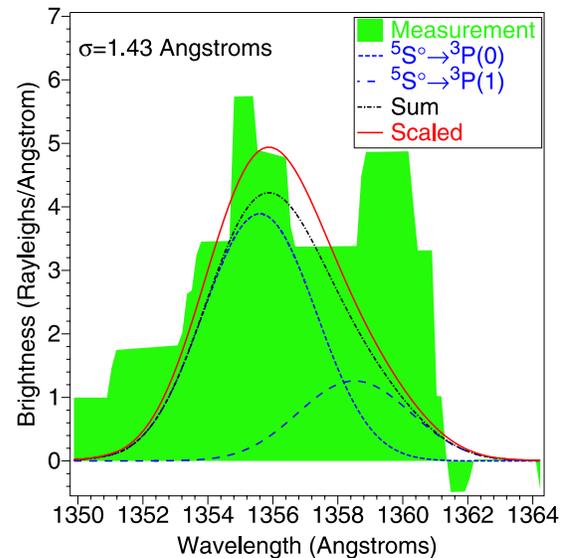


Figure 1. Measured, calculated and scaled brightness of the O I emissions around 1356 Å. The calculated brightness (for Gaussian lines with standard deviation $\sigma = 1.43\text{ Å}$) is shown for the $3s^5S^{\circ} \rightarrow 2p^4\ ^3P(0)$ (dotted line) and $3s^5S^{\circ} \rightarrow 2p^4\ ^3P(1)$ (dashed line) transitions, for their sum (dot-dashed line) and for this sum scaled by 1.17 (solid line).

Table 2. Selected CO Transitions, “g-Factors” and Predicted Emissions for a CO Column Density of $4.0 \times 10^{14} \text{ cm}^{-2a}$

Transition			Brightness (R)		
A $^1\Pi$ Level	X $^1\Sigma_g^+$ Level	Band Head (Å)	g-Factor	Fluorescence	Electron Impact
0	0	1544.5	0.52	20.8	10.0
0	1	1597.3	0.93	37.2	17.8
0	3	1712.4	0.40	16.0	7.7
0	4	1775.2	0.14	5.6	2.7
1	4	1729.6	0.65	26.0	15.2
1	5	1792.8	0.45	18.0	10.5
2	1	1525.9	0.04	1.7	1.4
2	2	1576.9	0.50	20.0	16.8
2	3	1630.6	0.42	16.8	14.1
2	5	1747.5	0.17	6.8	5.7
3	2	1542.5	0.47	18.8	18.4
3	5	1705.4	0.15	6.0	5.9
4	4	1611.5	0.08	3.2	4.3
4	6	1724.1	0.09	3.7	5.0
5	0	1392.6	0.36	14.4	7.4
5	3	1527.7	0.22	8.8	4.5
5	5	1629.1	0.18	7.2	3.7
5	7	1743.3	0.06	2.3	1.2
totals:				233.3	152.3

^a“g-factors”, $10^{-7} \text{ photons s}^{-1} \text{ molecule}^{-1}$. The electron impact predictions are for $\sigma = 1.43$ and scaling factor of 1.17.

[14] As *McPhate et al.* [1999] did not specify the emissions used, we have followed their stated rules to select the transitions shown in Table 2. The brightness of each line for a CO column density of $4.0 \times 10^{14} \text{ cm}^{-2}$ is calculated using equation (1). The sum of these is 233 R, consistent with the value of 230 ± 30 R quoted by *McPhate et al.* [1999]. Therefore we believe we have chosen either the same lines, or at least a very similar subset of lines, to those chosen by *McPhate et al.* [1999].

[15] Also shown in Table 2 is the brightness of each line that we calculate due to electron impact, for the same CO column density. These are determined by calculating the volume emission rate/molecule ($\text{photons molecule}^{-1} \text{ cm}^{-3} \text{ s}^{-1}$), which is equivalent to the “g-factor” in equation (1). The sum of 152 R implies that electron impact accounts for 40% (i.e., $152/(152+233)\%$) of the CO emissions. As the density of 4.0×10^{14} calculated by *McPhate et al.* is based on the assumption that all the emissions are due to fluorescence, the implication that only 60% of the emissions are due to fluorescence implies a CO column density of $2.4 \times 10^{14} \text{ molecules cm}^{-2}$ rather than 4.0×10^{14} , which is consistent with the measurement of *DiSanti et al.* [2001].

[16] This is a minimum estimate of the contribution from electron impact. The standard deviation $\sigma = 1.43 \text{ Å}$ was determined by finding the value which gave the best fit of our calculated CO lines to those in the synthetic spectrum plotted by *McPhate et al.* [1999], subject to the constraint that the total brightness for the selected lines be the same. The estimate of $\sigma = 1.43 \text{ Å}$ for the Gaussians fitted in Figure 1 corresponds to a full width at half maximum (FWHM) of 3.4 Å . *McPhate et al.* [1999] specify a “resolution” of $\sim 5 \text{ Å}$, suggesting that the value of 3.4 deduced from their fitted function is too small. If a larger σ is used, the calculated O I peaks in Figure 1 would have smaller maxima (as the area under the peak is proportional

to the volume emission rate), thus requiring a larger scaling factor and so giving larger estimates for the CO emissions.

[17] The implication is that in the previous calculations the density of CO in comet Hale-Bopp was overestimated because the contribution from electron impact was not included. However, the high value determined by *McPhate et al.* [1999] is supported by infrared measurements [*Brooke et al.*, 2003]. Therefore in the next section we repeat the fitting to the measured data made in the previous work, in order to investigate whether there might be an alternative explanation.

5. Fitting to the Measurements

[18] Here we repeat the fitting performed by *McPhate et al.* [1999] to their measurements, without and then with the electron impact contribution. This involves calculation of a synthetic spectrum by taking the “g-factors” in Table 2 and converting each to a Gaussian peak in relative brightness Å^{-1} . This synthetic spectrum is convolved with a rectangular function of width 3 Å , to incorporate the averaging over five 0.6-Å pixels applied by *McPhate et al.* [1999] to their experimental data. A least squares fit is then used to determine the absolute values of the synthetic spectrum.

[19] The measured spectrum was digitised from Figure 3 (bottom) of *McPhate et al.* [1999], taking only points that were not covered by the fitted spectrum. No attempt was made to guess the location of points that were underneath the fitted function. Therefore the method of digitisation should not bias the data towards the fitted function and so our fit is independent of the fit of *McPhate et al.* [1999].

[20] Initially we tested our method of fitting by emulating the calculation of *McPhate et al.* [1999]. for just a fluorescence contribution. The result of this process is shown in Figure 2, where the spectrum fitted to the experimental data

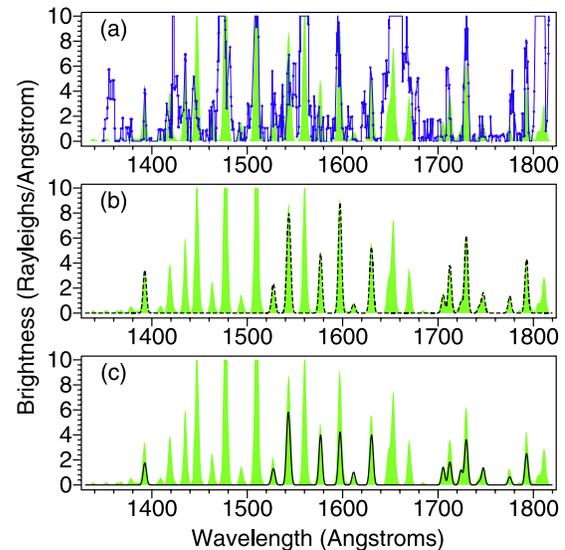


Figure 2. (a) Digitised measurements of CO emissions (filled circles) and the function fitted by *McPhate et al.* [1999] (shading). Calculated CO emissions (for $\sigma = 1.43 \text{ Å}$ and column density $4 \times 10^{14} \text{ molecules cm}^{-2}$) due to (b) fluorescence (dashed line) and (c) electron impact (solid line), with the function fitted by *McPhate et al.*

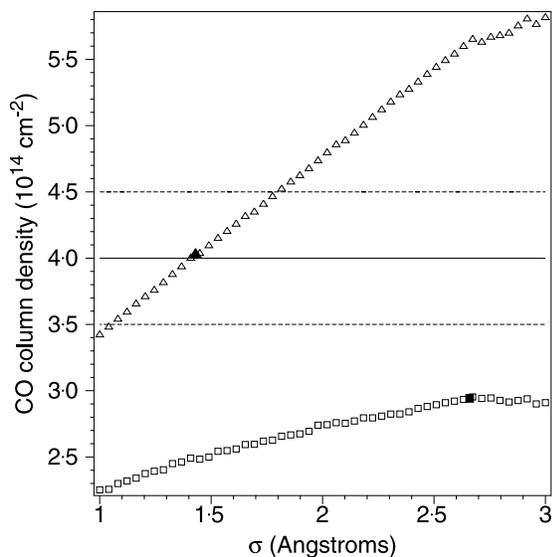


Figure 3. Deduced CO column density as a function of σ for fluorescence only (\triangle) and fluorescence plus electron impact excitation (\square), compared with the density deduced by McPhate *et al.* [1999] (solid line) and their error range (dashed line). The density determined in the case of Figure 2 (\blacktriangle) and the best fit with varying σ (\blacksquare) are also shown.

is plotted over the spectrum fitted by McPhate *et al.* The overall brightness for the current calculation is 235 R, which is very close to the value of 233 R for the fit by McPhate *et al.* [1999].

[21] Also shown in Figure 2 is the contribution for electron impact for the same CO density. This is consistent with the estimate above (for $\sigma = 1.43$ Å) that the electron impact contribution is $\sim 65\%$ of the fluorescence contribution. The new information is that there are some differences in the relative peak heights, as expected given that these will depend on the relative electron impact cross sections rather than photoexcitation cross sections.

[22] Given that the value of σ gives a FWHM that is less than the quoted resolution, we have repeated the calculation for a range of σ values. The results are shown in Figure 3, where the deduced CO densities for both fluorescence only and for fluorescence plus electron excitation are plotted as a function of σ . The fluorescent-only value of Figure 2 is highlighted, as is the “best fit” obtained for the case of fluorescence plus electron impact.

[23] Two apparent anomalies in this figure need explanation. It is expected that the deduced CO density would increase linearly with σ , as the least-squares fit will tend to match the amplitude of the peaks rather than the width and wider lines of the same amplitude will give greater brightness. The non-linearity for the combined case is due to the fitting to the O I line and the subsequent scaling to match the data (as illustrated in Figure 1). For a larger σ and the same total brightness, the amplitudes of the calculated O I lines are smaller, so a larger scaling factor is deduced. As this scaling factor is applied to the CO emissions, the contribution of the electron impact relative to the fluorescence becomes greater, giving a smaller fluorescence contribution and hence a lower calculated density. The

discontinuity at $\sigma \approx 2.65$ Å is related to the fact that the best fit is obtained at this value. When the fitted lines are wider than those measured, the wings of the line overlap with the higher values of the neighbouring line, hence corrupting the fit and so producing the discontinuities.

[24] A final observation is that the calculated CO lines in the wavelength range 1700–1800 Å are much smaller than the observed values. If the fit to the data is applied in just this range, the deduced CO densities are $6.4 \times 10^{14} \text{ cm}^{-2}$ for fluorescence only and $\sigma = 1.43$, and $(4.0 \pm 0.5) \times 10^{14} \text{ cm}^{-2}$ for fluorescence plus electron impact for $\sigma = 2 \pm 1$ Å. This inconsistency between results for the longer wavelengths and the full range suggests that there is a problem somewhere in the measurements, the method of analysis, or the CO branching ratios. This leaves open the possibility that the CO density in comet Hale-Bopp was indeed the value calculated by McPhate *et al.* [1999].

6. Conclusions

[25] A calculation of O I and CO fourth positive emissions produced by electron impact has been performed for the conditions of a measured UV spectrum of comet Hale-Bopp. The predicted O I emissions around 1356 Å agree well with the observations, giving confidence in the method of calculation and supporting the belief that this line is due entirely to electron impact. The brightness of the CO lines was calculated similarly and it was found that the predicted emissions due to electron impact are about 65% of those due to solar fluorescence. This suggests that electron impact excitation in comets is more important than was thought previously. As a previous study [McPhate *et al.*, 1999] ascribed all the CO emissions to solar fluorescence and deduced a CO density on this assumption, the inclusion of electron impact emissions implies a 40% reduction in the measured CO density. However, if the analysis is applied to just the longer wavelengths in the measured spectrum and electron impact is included, the calculated CO density is in agreement with that previous study.

[26] **Acknowledgments.** This work was funded by the Australian Research Council. Discussions which led to this investigation occurred as a result of financial support from DIISR under the International Sciences Linkages Program.

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