Rebuttal to “Comment on the paper “Comparison of the composition of the Tempel 1 ejecta to the dust in Comet C/Hale–Bopp 1995 O1 and YSO HD 100546” by C.M. Lisse, K.E. Kraemer, J.A. Nuth III, A. Li, and D. Joswiak”

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Abstract

This response is to address the comments made by Drs. J. Crovisier and D. Bockelee-Morvan concerning the spectral analysis of Lisse et al. [Lisse, C.M., Kraemer, K.E., Nuth, J.A., Li, A., Joswiak, D., 2007. Icarus 187, 69–86] of the mid-IR ISO SWS spectrum of Comet Hale–Bopp 1995 O1 taken on October 6, 1996, and to support the conclusions made in Lisse et al. concerning the positive detection of PAHs in this comet. We also present some additional information determined from the Deep Impact and STARDUST missions, demonstrating the presence of PAHs in other comets, to support the plausibility of the Hale–Bopp PAH detection.

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1. Introduction

The substance of the Comment and this Reply deal with the question of the presence or absence of spectral features in the 5–8 µm region of the Infrared Space Observatory (ISO) observations of Comet Hale–Bopp 1995 O1 (hereafter Hale–Bopp), the most active and well studied comet of modern times, taken in September–October 1996. Overall, we greatly appreciate the Comment submitted by Drs. Crovisier and Bockelee-Morvan—we are happy that some readers have taken the time to work through our analysis in detail, and we appreciate the discussion engendered. All have been useful, if not in solving the presence of PAHs in Hale–Bopp for all, then in agreeing that there is good spectral evidence for carbonates in the comet, in line with the latest STARDUST results (Wirick et al., 2007).

When reading Lisse et al. (2007), the Comment, and this Reply, it needs to be remembered that ‘PAH’ is an acronym denoting a mix of similar materials, and that the observed PAH IR emission features are due to resonant de-excitation of the poly-aromatic molecules following excitation of the electronic manifold by a UV photon. The PAH features are much broader than simple molecular lines often found in the near-IR, both because of the multiplicity of ro-vibrational modes in the large extended PAH molecules (e.g., PAH molecules of 100–800 amu have been found by STARDUST in their returned samples; see Sandford et al., 2006, SOM Fig. S3), and that they arise from a distribution of PAH compounds, not one single species. The expected emission features contain much of what a molecular spectroscopist would consider “continuum,” as well as sharply peaked features, complicating their detection using narrow line detection methods.

Another important point to note is that the relative strength of the different strong, relatively stable PAH-to-PAH features vary depending on whether the PAH molecule is ionized (the extended aromatic ring system can easily stabilize the loss of an electron, and in fact for some ring systems this is the preferred ground state) or neutral. We found only ionized PAH models fit the ISO data. This seems entirely physically consistent, as laboratory and theoretical estimates of PAH ionization lifetimes are on the order of seconds to minutes at 1 AU. It also explains why PAHs have been so difficult to detect with near-IR spectroscopy using the 3.2–3.4 µm complex, as ionized PAHs will have much weaker near-IR features than mid-IR features (see p. 75 of Lisse et al., 2007, and the discussion of the g-factor and total PAH production rates in Bockelee-Morvan et al., 1995).

2. Cometary PAHs

We know that PAHs exist in comets. In addition to the Spitzer 5–12 µm evidence for PAHs in Tempel 1 presented in Lisse et al. (2006, 2007), which is not in dispute nor repeated here for the sake of brevity, we show two additional pieces of evidence. The STARDUST sample return clearly shows evidence for PAHs in the samples returned from Comet 81P/Wild 2 (Fig. 1a; Sandford et al., 2006, Science and especially the associated supplementary on-line material). The mass spectrum of the STARDUST PAHs is broad, and form a complex of PAHs, similar to but with average size only 10–20% larger than used in our modeling. The Deep Impact experiment showed strong evidence for PAH lines in the spectra of not only the ejecta, shining by UV fluorescence in the same manner as PAHs in Hale–Bopp’s coma (Lisse et al., 2007, Fig. 2) but...
after Sandford et al. (2006). For completeness on the subject, we also direct the reader to potential Earth-based spectral detections of PAHs in the near-IR for Comet 1P/Halley 1986 by Baas et al. (1986) (but see also Bregman et al., 1987) and in Comets Halley, Bradfield, Brossen–Metcalf, and Levy by Bockelee-Morvan et al. (1995), but do not discuss them further here as this evidence has not been considered definitive to date.

A very fundamental and important question to answer is that if PAHs are present in Comets Wild 2 and Tempel 1 and throughout the ISM, where are they in the highly active and organics rich Comet Hale–Bopp? Are they sequenced, hidden inside other materials, or are they gone, destroyed by massive stellar flares in the T Tauri phase of the Sun, or in the accretion shock or spiral density shocks created by the giant planets as they form? A discussion on this topic was given on p. 83 of Lisse et al. (2007).

3. Data analysis

The fundamental difference between the method of Crovisier and Bockelee-Morvan is that our method attempts to understand the source of all contributions to the spectrum, not just high frequency features above a continuum. I.e., our $\chi^2$ procedure fits not one or two PAH features, as indicated in the Comment, but five predicted features simultaneously (at 6.1–6.3, 7.6–7.8, 8.5–8.7, 11.2–11.3, and 12.3–12.5 $\mu$m; Fig. 2), plus the associated non-zero continuum-like emission between them. Since the exact mix of PAH molecules in comets is still being determined (and may vary from comet to comet as well), the spectral features are somewhat mutable in terms of their central wavelength of emission (on the order of $\pm 0.1\mu m$), and in the width of the emission features (on the order of $\pm 0.05\mu m$). The PAH model we have utilized attempts to model this complex state of affairs by assuming a distribution of PAH molecule sizes with a mean size and ‘Gaussian width.’ This is of course a simplification of the real system; further complications will arise, if, as Sandford et al. discuss, the PAHs in comets are often heterocyclic, i.e. the aromatic rings contain also N and O atoms. We do agree that there are issues with this statistical PAH model and expect improvements in the modeling, and new results to be determined on the PAH species, with further modeling guided by the new STARDUST PAH results.

We worked with the October 6, 1996 SWS data only, as kindly provided by J. Crovisier in March 2000 to our group, and noted in the Comment. These data are presented in Crovisier (2000). (We have not opportunity, as of this writing, to work with the other datasets presented in the Comment, although, as we point out below, the only other useful dataset is the 26 September 1996 SWS spectrum.) The temperature corrected emissivity spectra and PAH model used are shown in Fig. 2. The original fluxes and subtly different scattered light removed fluxes are shown in Fig. 3.

Detection of PAHs in Hale–Bopp was not easy with the as-delivered spectrum ISO spectrum (Fig. 3). As we discussed on p. 75 of Lisse et al. (2007), the signal was relatively weak compared to the amount of scattered light contamination. No statistically significant PAH signal was found for the as-delivered comet spectrum, which contrasted significantly with the Deep Impact Tempel 1 results, and, along with the unusually large near-IR continuum, caused us to investigate this issue in some detail. Our first attempts at arbitrarily fitting the spectrum to a smooth baseline and subtracting this removed all flux at 5–8 $\mu$m. This is equivalent to the treatment applied by the authors of the Comment.

However, we knew this was patently incorrect because there is a substantial thermal emission component from the comet dust material—the strong thermal emission at 9–35 $\mu$m from silicate dust has a non-zero counterpart at 5–8 $\mu$m, although it is relatively weak because the dust is relatively cold ($\sim 210$ K) and the 5–8 $\mu$m wavelength region is well into the Wien law side of an 210 K black-body. It is critical to note that our compositional spectral modeling does not throw away any of the so-called “continuum” away, it instead determines the source of it at each wavelength (Lisse et al., 2006, 2007). The same materials that create the characteristic diagnostic emission peaks also creates the intervening continuum! By carefully allowing for how larger dust particles emit more “continuum” and less “peak” as they approach an optically thick radius, it is possible to detect the emission from the more weakly emitting “second tier” materials in comets, like water, PAHs, carbonates, metal sulfides, amorphous carbon, etc.,

![Fig. 1. Strong evidence for PAHs in comets. (a) PAH mass spectrum distribution for the Murchison meteorite, 5 IPDs, and STARDUST sample return track #16. Also shown are the chemical structures for the most commonly found PAH species in these samples. After Sandford et al. (2006). (b) Spitzer Space Telescope High time resolution two-dimensional spectroscopy of the Deep Impact ejecta, taken immediately after the impact of the spacecraft’s probe into the nucleus of Comet 9P/Tempel 1. The 5–9 $\mu$m emission detected from the comet at this time was dominated by direct thermal emission from hot ($\sim 1000$ K) PAHs at $\sim 5$ $\mu$m not seen in a quiescent comet, as well as emission in the usual 7.7–8.6 $\mu$m region. The PAH elevated temperature is consistent with the hot H$_2$O and CO$_2$ detected by the DI HRI-IR spectrometer (A'Hearn et al., 2005). Also demonstrated the detection of unusual “hot thermal PAH” line emission at 5–8 $\mu$m, seen in the high speed spectroscopic measures of the $\sim 1500$ K prompt hot gas plume emitted within the first few seconds after impact (Fig. 1b; Lisse et al., 2006). For completeness on the subject, we also direct the reader to potential Earth-based spectral detections of PAHs in the near-IR for Comet 1P/Halley 1986 by Baas et al. (1986) (but see also Bregman et al., 1987) and in Comets Halley, Bradfield, Brossen–Metcalf, and Levy by Bockelee-Morvan et al. (1995), but do not discuss them further here as this evidence has not been considered definitive to date.]

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after the dominant signal due to the emission from silicate materials is removed (Fig. 2b).

A careful fit of the scattered light component, by extrapolation of a proper solar model spectrum from optical and near-IR spectrophotometry was required to remove the dominant non-thermal components of the flux for this very high dust albedo (~40%) comet. *Note that in performing our modeling, we checked the effects of removing the scattered light, by allowing the amount of scattered light removed to vary within the errors of the optical/near-IR spectrophotometry and re-running the compositional modeling. We achieved the same best-fit model results and PAH detections for all values of the scattered light removal within the error bars.*

![Figure 2](image1.png)

**Fig. 2.** Emissivity spectrum for Comet Hale–Bopp. (a) As calculated from the 6 October 1996 ISO SWS spectrum by removing the coma scattered light and the gross temperature dependence of the dust thermal emission (black thin line). The PAH model utilized in Lisse et al. (2007) is shown for comparison (thick blue line). The PAH model has emission peaks at 6.1–6.3, 7.6–7.8, 8.5–8.7, 11.2–11.3, and 12.3–12.5 µm and non-zero emission throughout the 5–9 µm wavelength range. (b) PAH model as compared to the emissivity spectrum after all other mineral components have been accounted for, as explained in Lisse et al. (2007). While the fit is not perfect, emission in the wavelength regions predicted by our simple PAH emission model is clearly present.

We thus have serious concerns about the methods used by the authors of the Comment. Arbitrarily fitting a second order polynomial to the data is potentially dangerous, as it will remove much of the broad PAH features as well as the scattered light. While this technique should work for narrow band, strong molecular line features, it is incorrect for dealing with the broad PAH features. The authors of the Comment need to show one uniform non-PAH emission flux removal technique spanning the entire spectrum, and then do their fits on the data.

The ISO-PHT baseline calibration is known to be somewhat problematic, and the spectral data are of lower resolution, so we are not surprised at the difficulties stated by the authors in interpreting the PHT 27 September and 7 October datasets with respect to our results. We do not think we will be able to work with this data using our methodology because of the problems with the PHT data, and we do not believe the PHT data to be reliable in looking for faint, low contrast spectral features. However, in future work we will try our compositional modeling on the 26 September 1996 SWS spectrum, to treat it the same way we did the October 6 data, and see if there is good agreement between the two sets of results.

The authors of the Comment state “For comparison, we have listed in the same table the intensities of the features from the model of Lisse et al., evaluated from Fig. 3a of their paper (it should be noted that in this figure, the carbonates contribution is plotted with an increased scale factor of 2.0, and the PAH features with a scale factor of 1.0. C. Lisse, personal communication).” It is indeed correct that we amplified the carbonate (and only the carbonate) contributions by a factor of 2 for the purposes of presentation in Fig. 3a of Lisse et al. (2007). On the other hand, this author is not aware of how the model curves used in the Comment have been generated; we have not shared our model directly with the authors, and cannot be sure as to the fidelity of what is presented. There appear to be important differences in the two models—and it is important to note that we did our fits in emissivity space, i.e., after removal of scattered light and temperature effects via division by a blackbody function. We do know that the model we used, as shown in Fig. 2, and our model fits, as shown in Fig. 3 of Lisse et al. (2007), run through the data points + 2σ error bars for SWST06 at >95% level of significance. Coupled with the fact that there are no other known common constituents of comets that emit the IR flux detected at ~7.7 µm, we find this to be a compelling case for the presence of PAHs in Hale–Bopp.

Finally, we strongly disagree with the authors of the Comment in that the use of a $\chi^2$ fitting technique is certainly justifiable if one has reasonable input components, as have been determined using the STARDUST and Deep Impact experimental results, the derived models are clearly and completely described, one carefully checks the shape of the residuals after all other components are removed vs the expected emission features (Fig. 2), and one is careful not to over-interpret the results. Unlike all previous work we are aware of, we have listed the numerical values for the parameters of our fit and the resulting goodness of fit chi-squared statistic. The IR spectrum contains information, if we...
interpret it carefully, and our method certainly does look for the spectral features of the individual materials, as determined from representative laboratory spectra. We do indeed demand that the materials determined to be present show demonstrable spectral features—e.g., the ~6.8 μm feature of carbonates, the ~7.7 and ~8.6 μm feature of PAHs, the 9.8, 11.2, 19, 23.5, and 33.5 μm features of crystalline olivine, etc. The ease with which we were able to fit the thermal emission spectrum of Hale–Bopp (and now SW1 and SW3 as well), given the Tempel 1 compositional mix of representative cometary materials, and how well we have done in predicting the classes of materials found in the STARDUST sample return, demonstrates this.

But this was not possible except in hindsight, after the Deep Impact experiment had greatly clarified the problem by producing the most detailed mid-IR spectrum of cometary emission ever obtained.

As with any model, and with any remote sensing experiment, it is important to recall that there are important limitations to the approach used. These limitations, which include matters of abundance, uniqueness, and precision, along with the multiple techniques and physical checks we have utilized to reduce their effects and validate our work, are listed in detail on pp. 71–73 of Lisse et al. (2007). We have kept these clearly in mind when making our interpretations, which are discussed for the PAH component on p. 83.

4. Further work

We would like to state again that we are indebted to the authors of the Comment for their analysis and expertise. While we respectfully disagree with their conclusions and stand by our analysis, we appreciate the time it took to read our paper and examine our analysis in detail, and to search for evidence of not only PAHs, but carbonates, in their analysis, and take heart in the fact that they do find positive evidence for carbonates in their Table 1. Our work with the ISO Hale–Bopp data is only as good as it compares to other experiments, e.g. Spitzer comet measurements, the STARDUST sample return, etc. Also, we have now been provided by their group with the 26 September 1996 SWS spectrum, which we will analyze in the next year, using the same procedure as the 6 October 1996 SWS spectrum we reported on in Lisse et al. (2007), searching for confirmation of our analysis. When doing this, we hope to improve the mix of PAHs used to create the emission model presented in Lisse et al. (2007), following the new STARDUST results of Sandford et al. (2006).

One question which this discussion has engendered for us to investigate is: Is it possible that we could be seeing PAHs in absorption of the scattered sunlight from the optically thick dust deep down in the coma, e.g. at 7.6–7.7 μm? As for other comets, Hale–Bopp was observed by scattered sunlight and thermal re-radiation, and we had expected only emission features to be present, and proceeded with our interpretation accordingly. However, as the ISO SWS beam at 5–12 μm is ~20′′ × 20′′ (42,000 km × 42,000 km) at the comet, photons contributing to the observed spectrum arise from a substantial fraction of the coma. Unlike any other comet (with the possible exception of Halley’s inner coma), there were reports that the coma of this incredibly active comet was optically thick (e.g., Fernandez et al., 1999; Combi, 2000, and references therein). While our first thought is that the optically thick region of the coma is small and likely to be of minor total contribution, we think this is worthy of further study.

References