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Collision-Induced IR Emission Spectra of Impact-Heated Rare-Gas Clusters

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Emission spectra of mixed rare gas clusters, heated by impact with a hard surface at hypersonic velocities, are shown to extend into the near-IR and visible regimes. The emission is due to the transient dipole that arises during the collision of dissimilar atoms. The simulations are for a cluster that remains in the electronic ground state throughout the collision and use classical dynamics to determine the positions of the atoms vs time. The spectrum is computed as the Fourier transform of the (quantum mechanical) time rate of change of the dipole of the cluster. The time dependence of the dipole velocity is obtained by replacing the positions of the atoms by the computed classical functions of time. Taking the Fourier transform of the dipole velocity rather than of the dipole itself introduces a quantal correction with the result that the computed spectrum satisfies the oscillator sum rule. Binary collisions make the major contribution to the spectrum and there are hardly any caging effects. The spectral density of emitted photons is found to be thermal with a temperature that scales linearly with the impact velocity. Using the oscillator sum rules, this temperature is related to the deformation energy of the electronic charge cloud of the cluster. The hot cluster shatters and the fragments are in translational thermal equilibrium with a mean energy that scales linearly with the energy of impact. The temperature of the emitted light is, therefore, significantly lower than the translational temperature.

Introduction

Mixtures of rare gases at room temperatures absorb light in the far IR.[1−5] The dependence of the absorption on the gas density, the temperature and the chemical identity of the two rare gases ascertain that the absorption is due to a transient dipole that arises when two dissimilar atoms collide. The absorption line shape[6] rises from zero, peaks, and decreases exponentially at higher frequencies. On physical grounds we expect[4] the width of the absorption line (or the most probable frequency) to scale as the square root of the temperature. This is because the time scale for the motion of the transient dipole is the duration of the collision. This duration scales as a/v where a is the range of the intermolecular force and v is the velocity during the collision. The spectrum is determined by the range of frequencies that correspond, by the Fourier transform, to the motion of the dipole. Hence the spectrum is expected to scale as v/a or, for an ensemble, as $\sqrt{T}$, where T is the translational temperature. This is borne out by systematic experimental studies, e.g., ref 2. Results for the Ar−Xe are shown in Figure 5 below.

The theory of collision-induced absorption has been extensively developed and has been applied not only to atoms but also to collisions of molecules. Currently, the theory offers a parametrized form of the line shape that can accurately fit experimental results. The purpose of our work is to provide computational results that can serve as a guide for an experiment on a hot mixed cluster. We, therefore, need to compute the spectrum from the dynamics. The cluster has many atoms so it is far simpler to implement a classical dynamics computation of the time evolution of the cluster than a quantum mechanical one. In its present form, the theory of collision-induced absorption computes the spectrum from the time evolution of the transient dipole that arises during the collision of dissimilar atoms. This works well if the computation is quantum mechanical. Often, however, the dipole is taken to evolve along a classical trajectory. Then there is an inherent problem. It is that the results lead to an oscillator sum whose value vanishes identically. The theory of collision-induced absorption is usually cast in terms of spectral moments. The oscillator sum rule is equivalent to the first spectral moment. So the problem is that the first spectral moment is identically zero when the time dependence of the transient dipole is computed for motion along a classical trajectory. There are good reasons to expect that for heavy atoms the first spectral moment will not be large. This is because the leading contribution to this moment is of the first order in Planck's constant h.[7,8] Our theoretical interpretation of the results hinges, however, on the first spectral moment being finite. We have found that it is possible to overcome the problem and to use classical mechanics to compute the collision dynamics and yet to have a finite first spectral moment.[8] In the usual approach one starts with the dipole as function of the nuclear coordinates and computes a time dependent dipole by letting the coordinates evolve along a classical trajectory. We start from the time rate of change of the dipole.[9] This dipole velocity is computed from the quantum mechanical Heisenberg equation of motion. The resulting dipole velocity is a function of the nuclear coordinates and it is at this point that we take the nuclear coordinates to evolve in time according to classical dynamics. The difference with the usual approach is that the quantum mechanically computed dipole velocity has a term, of order h, that is not present in the classical dipole velocity. This term can be explicitly identified as giving rise to a finite first spectral moment.

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In view of its intended applications, the theory of collision-induced absorption has been formulated with special reference to systems in thermal equilibrium. It is not necessary to do so but the established approach early on makes the assumption of thermal equilibrium. Our intended application is to systems not necessarily in equilibrium. So the more minor difference with the conventional approach is that we do not require nor do we make an equilibrium assumption. Rather, we follow the dynamics.

The system we deal with is a cold molecular cluster impacting a hard surface at a hypersonic velocity. Following the impact, the cluster heats up because the initially directed velocity is rapidly randomized by collisions within the cluster.[10−13] In this paper we discuss the emission of light from this hot and condensed medium. We begin with a number of observations about this unusual state of matter. The first is that soon after impact the hot cluster shatters, with fragments receding from the surface in all directions. Shattering is prompt but not immediate: For not very small clusters, the time interval between the initial impact and the fragmentation is sufficient for several intracluster collisions to take place. The most direct evidence for intracluster collisions is that both experiment, e.g., ref 14, and simulations[12] show that the translational motion, which before the impact was highly directed and tightly defined in magnitude, has reached thermal equilibrium. In particular, the velocity distribution of the emerging fragments does not appear to depend on the direction of observation with respect the surface normal and its distribution is Boltzmann-like. There is significant energy loss to the surface.[15] Still, the fraction of the initially directed kinetic energy that appears as the random kinetic energy of the fragments is high. There is also some experimental evidence[16] and simulations[11,17,18] showing that high-barrier chemical reactions can take place within the impact-heated cluster. The relative velocity within the heated cluster is comparable to the initial velocity. At thermal and hyperthermal velocities the principle of exponential gap[4] suggests that equilibration of internal modes may be incomplete and require more than a few collisions. But for hypersonic impact there is computational evidence for extensive vibrational heating. There is both experimental[19,20] and computational[21] evidence for electronically nonadaiabatic processes. At thermal and hyperthermal velocities one observes primarily charge separation, with the autoprotolysis of water, $H_2O + H_2O \rightarrow H_3O^+ + OH^-$ being best studied.[22] For a very recent report of autoprotolysis of nitric acid, see ref 23. At higher energies there is copious emission of electrons with a thermal distribution of their kinetic energy.[20]

In summary, the impact-heated cluster has a fleeting existence as a medium in which very hot collisions take place. We want to study light emission during that interlude.

The second observation about cluster impact is that under the conditions described above we should expect electronic excitation to occur. To the best of our knowledge this has not been observed and attempts to experimentally detect light from the hot cluster have so far not been productive. One reason could be that the surface, which is still close, effectively quenches any electronic excitation. A way to reduce such a quenching is to consider emission in the near-IR. A possible mechanism that could lead to such an emission is the transient dipole that is associated with the collision of dissimilar atoms. This paper shows that such a collision-induced emission from the hot cluster can peak in the near-IR or even in the visible and hence can be detected over the blackbody background.

The expectation that also at higher velocities the spectrum peaks at a frequency that scales as the square root of the translational temperature is borne out by the detailed computations. This means that heating a mixture in an ordinary shock tube[24] will not give rise to an easily discerned signal because the translational temperatures that can be reached are only about an order of magnitude above room temperature. The final translational temperature of the fragments of the hot cluster scales as the impact energy.[13] Therefore, the mean energy of the emitted photons scales as the impact velocity. It follows that the emitted radiation is not in equilibrium with the translational motion. We have argued[8] that the radiation temperature characterizes the electronic deformation during the collision. The computation of a collision-induced emission assumes that the system maintains its ground electronic state throughout the collision. There are both experimental and theoretical reasons to expect that this assumption will be qualitatively wrong for impacts at velocities above 10 km s^{-1}. In this paper we restrict our consideration to ordinary collision-induced emission. We are, however, extending our work to characterize emission from electronically excited states that are accessed during the collision.

TABLE 1: Lennard-Jones 12,6 Potential Parameters

	well depth ϵ, kJ mol^{-1} (range parameter σ, Å)	
	Ar	Xe
Ar	0.996 (3.41)	1.377 (3.735)
Xe		1.904 (4.06)

There is also a transient dipole that arises when cluster atoms collide with the surface. We do not include a possible emission from this dipole in the computations. The reason is that if, as assumed by the experimentalists, the surface quenches the electronic emission from the cluster, then it will also quench the emission due to surface-cluster motion.

The computation of the trajectories for cluster impact follow established procedures[25] and is reviewed next. In particular we show the rapid rise of the random part of the cluster kinetic energy after the impact. To compare experiments at different velocities of impact, we discuss the scaling of the dynamics with the initial velocity. At our collision energies, which are much above the well depth of the atom−atom potential, the useful variable is not the time t after the initial impact but the mean path of a rare gas atom, roughly given by vt, where v is the impact velocity. The details of the computation of the spectrum are provided with special reference to why we compute the spectrum from the dipole derivative. The scaling of the dynamics with vt is shown to hold also for the dipole, and therefore, the frequency spectrum scales as ν/v. The functional form for the potential and the dipole function[26,27] are validated by comparing with known results[2,28] for collision-induced absorption of rare gases at ordinary temperatures. The emission spectra computed for impact velocities in the hypersonic range are presented and shown to be thermal-like.

Molecular Dynamics Simulations

Mixed rare gas clusters were equilibrated at 30 °K using an established procedure.[25] The atom−atom potentials were of the Lennard-Jones 12,6 functional form with parameters fitted to results of high equality.[29] The potential was a sum of atom−atom contributions. Clusters of different compositions and sizes were studied. The results reported below are for a 256 atom cluster that is an equal mixture of Ar and Xe. The parameters for the Ar/Xe cluster are given in Table 1. Up to this point

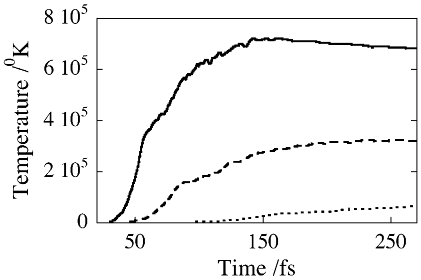

Figure 1. Translational temperature of the cluster vs time in femtoseconds, at three impact velocities: 5 (dotted line), 10 (dashed line), and 15 (solid line) km s^{-1}. The temperature is computed from the random part of the kinetic energy of the atoms as discussed in the text. The simulation begins with a cold, equilibrated cluster of 256 atoms, half Ar and half Xe, at a fixed distance from the surface. At time zero the center of mass of the cluster is given an additional velocity, the velocity of impact, in a direction normal to the surface. A higher velocity of impact makes the cluster reach the surface earlier. The slight cooling of the cluster, seen most clearly in the plot for the collision at 15 km s^{-1} after about 150 fs, and for all impacts in Figure 2, is due to the center of mass of the cluster beginning to recede from the surface. This results in a conversion of about 5% of the random kinetic energy to directed energy of the center of mass. The resulting decrease in the entropy is more than compensated by the increase due to the atoms moving out into all possible spatial directions.

what we do is very similar to the recent report on collision-induced absorption in cold clusters.[28] In our case, following equilibration, the center of mass of the cluster was given a velocity in a direction normal to a hard surface. The potential between the atoms and the surface is Lennard-Jones 12,6 with a well depth $\epsilon = 0.996$ kJ mol^{-1} and range parameter $\sigma = 5$ Å. Unlike the treatment in ref 13, here we do not include a friction with the surface so that there is no energy loss.

After a short, subpicosecond, compression interlude, an impact at a hypersonic velocity with the surface leads to a complete shattering of the cluster. The classical equations of motion for the position of the atoms were integrated until the velocities of all atoms settled to a constant value indicating no further collisions.

As a result of the impact, the initially directed kinetic energy of the cluster is very rapidly randomized. Figure 1 shows the rapid rise of the random part of the kinetic energy of the atoms vs time since the beginning of the trajectory. The trajectories all start at a given distance from the surface so that lower energy impacts reach the cluster later. By “the random part of the kinetic energy” we mean, as usual, the kinetic energy with respect to the center of mass

$$T_{\text{random}} = \sum_{\text{all atoms}} \frac{1}{2} m(v - v_{\text{center of mass}})^2 \qquad (1)$$

This is the part of the kinetic energy of a body that is equivalent to a temperature and Figure 1 reports the kinetic energy in terms of its temperature equivalent, $T_{\text{random}} = (3/2)k_B T \sum_{\text{all atoms}} 1$. We reiterate that experiments verify that after the shattering of the cluster the fragments disperse in all directions and have a Boltzmann distribution. In ref 12 we have suggested a model showing that the facile approach to equilibrium is due to the random packing of the atoms in the cluster.

To depict results at different velocities of impact on a common scale, we note that the hot atoms collide essentially as hard spheres so that the duration of a collision is very short. Most of the time the atoms are not interacting and so we use a distance scale where the distance time is velocity of impact times the time that elapsed since the first atom hit the surface. we

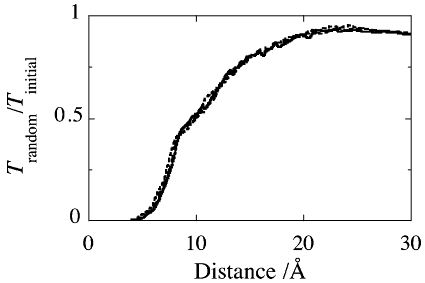

Figure 2. Reduced representation of the cluster kinetic energy. For different velocities of impact, the random part of the kinetic energy of the atoms, eq 1 is measured in units of the initial, directed, kinetic energy of the cluster, eq 2. In this figure we do not allow any energy transfer to the surface to show that essentially the entire impact energy is randomized. If dissipation of energy is allowed (see, e.g., refs 13 and 15), the random part of the kinetic energy of the atoms is lowered. The abscissa is a distance scale, in Å, obtained by multiplying time by the impact velocity. On this scale, the dynamics unfolds essentially independently of the energy of impact. Of course, this is only so at such impact energies that very much exceed the binding energy of the cluster. This is the scaling expected for hard sphere collisions.[12,31]

also scale the random part of the kinetic energy by the initial value of the kinetic energy. Because the cluster is initially quite cold, the initial kinetic energy is the energy of the center of mass motion

$$T_{\text{initial}} = \frac{1}{2} v_{\text{impact velocity}}{}^2 \sum_{\text{all atoms}} m \qquad (2)$$

With the scaling of energy and time we are able (see Figure 2) to bring different trajectories to a common reduced plot. This is of importance to us because we will want to scale the dipole function and the scaling of the dynamics is a prerequisite for being able to do so. For reference below also note that Figure 2 shows that the final translational temperature of the atoms scales almost exactly with the initial kinetic energy, meaning, cf. eq 2, that the final translational temperature scales as the square of the impact velocity.

The short range part of the dipole of a pair of different rare gas atoms as a function of the interatomic distance can be accurately determined by quantum chemical computations.[27] The collision-induced absorption spectrum computed for mixtures at room temperature is sensitive also to the long-range part of the dipole,[26] a part that has a sign opposite to the short-range component. We have used the dipole function with parameters adjusted to best fit the room-temperature CIA spectrum of Ar–Xe mixtures.[26] Our computations are for higher collision velocities and our computed spectrum does not appear to show a significant dependence on the detailed form of the long range part of the dipole. The only parameter that is found to be important is the range of the atom–atom repulsion. The dipole of the entire cluster is taken to be the (vector) sum of the contributions of the individual pairs. This is in part due to individual collisions often not overlapping in time. Figure 3 shows the cluster dipole vs time during a short time interval. It is clear that it is dominated by contributions of two independent collisions, each lasting about 10 fs. In the figure we resolved the two contributions to emphasize not only how little they overlap but also to show that the dependence of time of each peak is essentially that of two colliding atoms isolated from their environment. One could think that in view of the high density there can be caging effects. These would be reflected in a time dependence where the two atoms will not immediately separate but would undergo a secondary or even a tertiary

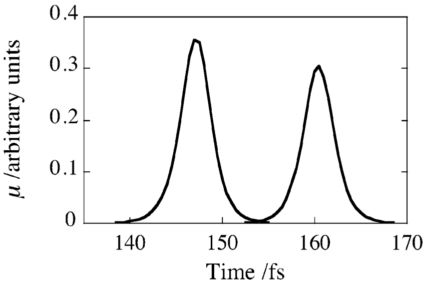

Figure 3. Time dependence of the dipole of two pairs of dissimilar atoms in the cluster in a short time interval during the impact at a velocity of 10 km s^{-1}. There are many small contributions due to pairs of atoms that fly-by but do not get close to one another. The large contributions are from binary collisions that are nearly head-on. The plot shows two such peaks, showing that they hardly overlap in time and that, as expected, they are about Gaussian in shape, with a full width of about 10 fs. That such peaks have no secondary peaks in their wings shows that the colliding atoms are not caged.

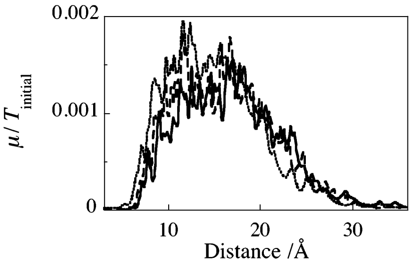

Figure 4. Cluster dipole vs the same distance scale as used in Figure 2, at three impact velocities: 5 (dotted line), 10 (dashed line), and 15 (solid line) km s^{-1}. By counting the peaks, one can judge that there are a few dozen close-in collisions that make the dominant contribution to the dipole. The dipole goes to zero when collisions cease due to the shattering of the cluster.

collision before they recede.[30] We searched for such events but among the dozens of binary events that lead to a significant peak in the cluster dipole vs time, there were typically only a few encounters. Even the rare caging events consisted in only two collisions with the second peak being much smaller than the primary one. This is consistent with what we found for dissociation of diatomic molecules embedded in rare gas clusters.[31] At the high velocities of interest there is essentially no caging. The binary nature of the cluster dipole also allows us to scale its time dependence in the same manner shown for the kinetic energy in Figure 2. The results are shown in Figure 4. The scaling does not quite allow different impact velocities to fall on a common curve, but the deviations are not large and the width in time clearly scales as a/v, where a is a distance factor and v is the collision velocity.

The standard classical theory of CIA obtains the spectrum from the Fourier transform of the dipole vs time. We, however, proceed otherwise. First we evaluate the quantum mechanical time rate of change of the dipole function. This brings in a quantum mechanical correction term that is central to our needs. To see this, consider the simple case of an atom−atom collision at a zero impact parameter so that the internuclear axis is not rotating. Then, if we treat the nuclear motion classically, the electrons track the nuclei:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mu(R) = \{\mu(R),K_{\mathrm{N}}\} = \mu'(R)\frac{\mathrm{d}R}{\mathrm{d}t} \qquad (3)$$

Here the curly brackets are those of Poisson and K_{N} is the kinetic energy of the nuclei. In an off-center collision there is also a contribution from the rotation of the interatomic axis. In the quantum mechanical Heisenberg equation of motion there is an additional term

$$\frac{\mathrm{d}}{\mathrm{d}t}\mu(R) = (\mathrm{i}\hbar)^{-1}[\mu(R),K_{\mathrm{N}}] = \mu'(R)\frac{P_{\mathrm{R}}}{M} - \mathrm{i}\hbar\frac{\mu''(R)}{2M} \qquad (4)$$

where P_{R} is the nuclear momentum operator and M is the reduced mass. $\mu''(R)$ is known as the electrical anharmonicity. Due to the electric anharmonicity, the change of the electronic charge distribution does not quite track the nuclear velocity.

The reason that the (purely imaginary) quantum mechanical correction term in eq 4 makes a qualitative difference is that under time inversion it has a different symmetry than the first term. Time enters in when we use a classical trajectory to generate the interatomic distance. R becomes a classical function $R(t)$. Under the inversion $t \rightarrow -t$ the classical momentum changes sign. Taking the origin of time at the distance of closest approach, $R(t) = R(-t)$, so under time inversion the classical, $\mu'(R)\ \mathrm{d}R/\mathrm{d}t$, term has an odd parity whereas the sign of the quantum correction is unchanged.

Given the (quantum mechanical) time rate of change of the dipole of the cluster, the rest of the computation is classical. The time rate of change of the dipole of the cluster is made into a classical function of time by replacing the operator R and functions thereof by the classical trajectory as determined by the molecular dynamics simulations. This cluster dipole velocity is then Fourier transformed using a standard fast Fourier transform routine

$$\dot{\mu}_{\mathrm{q}}(\nu) \equiv \int_{-\infty}^{\infty} \exp(2\mathrm{i}\pi\nu t)\dot{\mu}_{\mathrm{q}}(t)\ \mathrm{d}t \qquad (5)$$

The subscript q on the dipole function is to emphasize that the dot on the dipole function means a quantum mechanical time derivative. The reason for the need to emphasize this point is the familiar theorem that the Fourier transform of a time derivative is easily expressed in terms of the Fourier transform of the original function. If $\mu(\nu)$ is the transform of $\mu(t)$

$$\mu(\nu) = \int_{-\infty}^{\infty} \exp(2\mathrm{i}\pi\nu t)\mu(t)\ \mathrm{d}t \qquad (6)$$

then the transform of $\dot{\mu}(t)$ is $2\mathrm{i}\pi\nu\mu(\nu)$. But the function of time, $\mu(t)$, that is in the integrand of eq 6 is $\mu(R(t))$. So its time derivative, $\dot{\mu}(t)$, is $\mu'(R)\dot{R}$, which is the classical time rate of change of the dipole. In other words, it is not the case that $\dot{\mu}_{\mathrm{q}}(\nu)$, defined by eq 3 as the Fourier transform of $\dot{\mu}_{\mathrm{q}}(t)$, is given by $2\mathrm{i}\pi\nu\mu(\nu)$. Rather, there is a second term, the transform of the quantum correction in eq 4

$$\dot{\mu}_{\mathrm{q}}(\nu) = 2\mathrm{i}\pi\nu\mu(\nu) + \mathrm{i}\hbar\varsigma(\nu) \qquad (7)$$

where the quantum correction in the frequency domain is given by

$$\varsigma(\nu) \equiv \int_{-\infty}^{\infty} \exp(2\mathrm{i}\pi\nu t)(\mu''(R(t))/2M)\ \mathrm{d}t \qquad (8)$$

and $2\mathrm{i}\pi\nu\mu(\nu)$ is the Fourier transform of the classical time derivative $\dot{\mu}(t) = \mu'(R)\dot{R}$.

Both terms in eq 7 are determined from the time variation of the dipole along a trajectory. $\mu(\nu)$ is determined using eq 6 with $\mu(t) = \mu(R(t))$ and $\varsigma(\nu)$ is determined from eq 8. The dipole function used is the vector sum of the contribution of all pairs of different atoms. The final stage requires that all these terms are added coherently; that is, we need to compute $|\dot{\boldsymbol{\mu}}_{\mathrm{q}}(\nu)|^2$. We find that cross terms due to (quantal) interference of different

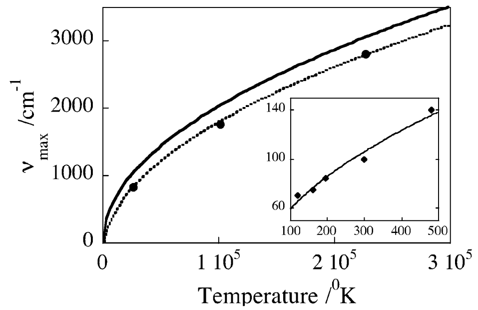

Figure 5. Most probable frequency in the collision-induced absorption spectrum of the cluster, points, vs the translational temperature at three impact velocities: 5, 10, and 15 km s^{-1}. The dashed line is the fit to a $\sqrt{T}$ dependence. The inset shows the experimental results from ref 2 at ordinary temperatures. The solid line is a fit of the experimental results to a $\sqrt{T}$ dependence. This solid line is then extrapolated over 3 orders of magnitude, as shown in the main plot.

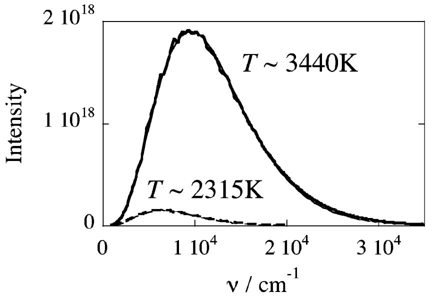

Figure 6. Computed intensity of the collision-induced emission of the hot cluster, (proportional to $\nu^2|\dot{\mu}_q(\nu)|^2$), vs frequency. The results are at impact velocities of 5 and 10 km s^{-1}. The light dashed line is the fit to a thermal distribution as given by eq 10.

pairs of atoms tend to average out so that for practical purposes one can approximate

$$|\dot{\boldsymbol{\mu}}_q(\nu)|^2 = |\sum_{ij\text{ pairs}} (\dot{\boldsymbol{\mu}}_{ij})_q(\nu)|^2 \cong \sum_{ij\text{ pairs}} |(\dot{\boldsymbol{\mu}}_{ij})_q(\nu)|^2 \qquad (9)$$

Most pairs of dissimilar atoms do not ever get close enough so that their dipole moment is only weakly varying, and these contribute to the very low frequencies. As we discuss next, this low-frequency contribution is masked by the density of state of photons that makes the emission spectrum proportional to $\nu^2|\dot{\boldsymbol{\mu}}_q(\nu)|^2$.

The light emitted by an accelerating dipole $\mu(t)$ is determined by $|\ddot{\mu}|^2$,[32] where, as above, the dots indicate the time derivative. The power emission at a particular frequency ν is computed by squaring the Fourier transform of $\ddot{\mu}$. It is here that we use the familiar theorem[33] to write this transform as $(2\pi)^2\nu^2|\dot{\mu}_q(\nu)|^2$, where $\dot{\mu}_q(\nu)$ is the Fourier transform of the quantum mechanical dipole velocity $\dot{\mu}_q(t)$; see eq 7. In the standard theory of collision-induced light emission the emission spectrum is written as $(2\pi)^4\nu^4|\mu(\nu)|^2$, where $\mu(\nu)$ is the Fourier transform of the time dependent dipole $\mu(t) = \mu(R(t))$. The point, as discussed above, is that these two expressions are not equal because $\dot{\mu}_q(t) \neq \mathrm{d}\mu(t)/\mathrm{d}t = (\mathrm{d}\mu(R)/\mathrm{d}R)\mathrm{d}R(t)/\mathrm{d}t$. One can consider the further refinement of computing the dipole acceleration quantum mechanically and taking its Fourier transform. This introduces higher order quantum corrections that scale as higher powers of $\hbar$. The next correction to the even function of the frequency, $\varsigma(\nu)$, scales as $\hbar^3$ and is negligible for fast moving heavy atoms. Hence, for our purpose, the first quantum correction, a correction that is order of $\hbar$ (see eq 7), is sufficient.

Computed Spectra

The first check is that the computations are consistent with the known results for collision-induced absorption. Figure 5 shows the maximum of the absorption for computations at different impact velocities. The plot is vs the final translational temperature of the cluster. Two notions are needed to justify this manner of plotting. The first is that equilibration of the kinetic energy after impact is sufficiently fast so that the translational temperature is a good measure for the relative kinetic energy at which collisions occur. This requirement is aided by the observation that absorption or emission must occur at the later stage of the impact. The reason is that it is collisions where the colliding atoms move with a higher relative velocity that contribute more heavily to the spectrum. This is because the spectrum emphasizes higher frequencies because the low frequencies are weighted down by the density of states factor of the photons. The higher frequencies originate from faster collisions. Early on during the impact most pairs are still moving with a low relative velocity. It requires that about half of all atoms reverse the sign of their velocity before the relative velocity is high. The second ingredient in Figure 5 is that the time dependence of the dipole scales as $1/v$, where v is the impact velocity. This has been shown in Figure 4. Combining the two arguments, we expect the most probable absorption frequency to scale as $\sqrt{T}$. The points in Figure 5 are the results of the simulations and the dashed line is the best fit to $\sqrt{T}$. The solid line is the best fit to the room-temperature observed absorption spectra,[2] extrapolated to the temperature range of interest. (The fit to the room-temperature data is shown as an inset in Figure 5.) It is remarkable how an extrapolation extended over more than 3 orders of magnitude of the temperature works so well.

The results shown in Figure 5 validate our working hypothesis. At the high relative velocities within the ultrahot cluster, collision-induced spectra will move in frequency toward the near-IR and the visible range. If all that one wants are the most probable absorption frequency or the width of the spectrum, we can take the scaling established around room temperature[2] and extrapolate.[34]

The actual simulations are needed to get the entire line shape for the emission spectrum. This is shown in Figure 6. The first observation is that the spectrum peaks at the near-IR but extends into the visible regime. It should, therefore, be experimentally possible to distinguish such emission from the background blackbody radiation.

Figure 6 also shows a fit, dashed line, of the frequency dependence to a thermal distribution[35]

$$(2\pi)^2\nu^2|\dot{\mu}_q(\nu)|^2 \propto \nu^4 \exp(-h\nu/k_BT) \qquad (10)$$

The fit is so close that the dashed line is only visible when the Monte Carlo noise of the simulations makes for a small kink in the computed results. We can eliminate much of this noise by generating several runs where, for example, we vary the initial orientation of the cluster with respect to the surface. When we compute a spectrum averaged over several runs, the fit is indistinguishable from the simulations. Elsewhere[8] we discussed why we expect the emission spectrum to be thermal and the results of the simulations are in good accord with our theoretical considerations.

The temperature T in eq 10 is high, as is to be expected for a spectrum that extends into the visible range. This temperature scales linearly with the impact velocity. The temperature of the emitted radiation is high but it is much lower than the translational temperature. (The translational temperature scales linearly with the impact energy.) What does the radiation temperature measure and why is it low compared to the temperature of the cluster as measured by the (random) kinetic energy of the atoms? It is in discussing these points, next section, that our earlier considerations about quantum corrections are needed in an essential way.

Sum Rules and Electronic Temperature

Spectral moments are determined by commutators with the Hamiltonian.[36] This was recognized very early on in the theory of collision-induced absorption.[7,37] However, because the intended applications were to systems in thermal equilibrium, the theory was developed by taking full advantage of the equilibrium assumption. For our purpose we want to compute the spectrum and its moments from the dynamics. It is indeed the case, as discussed below (see also Figure 6), that the resulting spectrum is very nearly that of a system in translational equilibrium, but we wanted this as a conclusion rather than as an assumption. Furthermore, it very much simplifies the computation if the dynamics is classical. Herein lies the problem. Say that the spectrum is computed in terms of the Fourier transform of the transient dipole along a classical trajectory. Then the first oscillator sum rule, the one known as the Thomas−Reiche−Kuhn sum rule in atomic spectroscopy, vanishes identically. For this reason we compute the Fourier transform of the quantum mechanical time derivative of the dipole. As discussed above, this introduces an additional (small) term, quantum mechanical in origin; see eq 7. The time evolution of the quantum mechanical time derivative of the dipole can be evaluated along a classical trajectory. The resulting spectrum has a finite value for the first oscillator sum rule.[8] The second oscillator sum rule for a vibrotational transition that is not accompanied by a change the electronic state is

$$\sum_{v'}(E_{v'} - E_v)f_{vv'} = \frac{2m_e}{\hbar^2}\langle v|([H,\mu(R)])^2|v\rangle$$
$$= 2m_e\left\langle v\left|\left(\frac{d\mu(R)}{dt}\right)^2\right|v\right\rangle \qquad (11)$$

Here $f_{vv'}$ is the oscillator strength for the change in the state of motion of the atoms

$$f_{vv'} \equiv \frac{2m_e}{\hbar^2}(E_{v'} - E_v)|\langle v'|\mu(R)|v\rangle|^2 \qquad (12)$$

m_e is the mass of the electron, $|v\rangle$ and $|v'\rangle$ are the initial and final states of the relative motion of the atoms, with energies E_v and $E_{v'}$, respectively. The photon frequency is $h\nu = E_{v'} - E_v$. (For reference below, note that emission corresponds to negative frequencies.) The dipole moment (vector) $\boldsymbol{\mu}(R)$ is the expectation value of the electronic dipole operator in the ground electronic state, $\boldsymbol{\mu}(R) \equiv \langle e|\boldsymbol{\mu}|e\rangle$. The dipole moment $\boldsymbol{\mu}(R)$ is time dependent because the electronic charge distribution deforms during the collision. The deformation vanishes when the (neutral) atoms are far apart and it also vanishes in the united atom limit. The kinetic energy of this deformation

$$i\hbar\frac{d\boldsymbol{\mu}(R)}{dt} = i\hbar\frac{d\langle e|\boldsymbol{\mu}|e\rangle}{dt} = \langle e|[\boldsymbol{\mu},H]|e\rangle = \langle e|[\mu,K_N]|e\rangle =$$
$$[\boldsymbol{\mu}(R),K_N] \qquad (13)$$

is, in the Born−Oppenheimer approximation, entirely due to the nuclear motion. The reason is that the total Hamiltonian H is the sum of the electronic Hamiltonian H_{el} and the nuclear kinetic energy operator K_N, $H = H_{el} + K_N$. The electronic ground state is a stationary state of H_{el} so that $\langle e|[\boldsymbol{\mu},H_{el}]|e\rangle = 0$. In the Born−Oppenheimer approximation one can write $\langle e|[\boldsymbol{\mu},K_N]|e\rangle = [\boldsymbol{\mu}(R),K_N]$. It is the kinetic energy of the electronic deformation that is measured by the second oscillator sum rule

$$\sum_{v'}(E_{v'} - E_v)f_{vv'} = \frac{2m_e}{\hbar^2}\sum_{v'}(E_{v'} - E_v)^2|\langle v'|\mu(R)|v\rangle|^2$$
$$= \frac{2m_e}{\hbar^2}\langle v|([H,\mu(R)])^2|v\rangle$$
$$= 2m_e\left\langle v\left|\left(\frac{d\mu(R)}{dt}\right)^2\right|v\right\rangle =$$
$$4\left\langle v\left|\frac{1}{2}m_e\left(\frac{d}{dt}\langle e|\mu|e\rangle\right)^2\right|v\right\rangle \qquad (14)$$

It requires no further theory to conclude that the second oscillator sum can be used to determine the mean (over all internuclear distances R) kinetic energy of the charge deformation. The second oscillator sum is, up to constants, the same as the second moment of the spectrum (provided that we sum over both emission and absorption). The mean kinetic energy of the charge deformation can, therefore, be computed directly from the spectrum. We, however, want to characterize this kinetic energy by a temperature. This is not essential, but it is instructive to look at the numbers that come out.

To introduce the notion of a temperature, we recall that observed or computed collision-induced spectra can be well characterized by the first three moments of the spectrum. The zeroth moment is just the area under the spectrum. The first spectral moment equals, up to constants, the first oscillator sum. It is here that we need, in an essential way, our computed first moment to be finite. The second spectral moment equals, up to constants, the second oscillator sum. By using the procedure of maximal entropy, we have shown[8] that given the first three moments the absorption coefficient $|\epsilon(\nu)|^2$ has the form

$$|\epsilon(\nu)|^2 = (S_0\beta/2)\exp(-\beta|\nu - \alpha|) \qquad (15)$$

where S_0, α, and β are determined by the first three spectral moments

$$\int_{-\infty}^{\infty}(S_0\beta/2)\exp(-\beta|\nu - \alpha|)\,d\nu = S_0$$
$$\int_{-\infty}^{\infty}(S_0\beta/2)\nu\exp(-\beta|\nu - \alpha|)\,d\nu = \alpha S_0$$
$$\int_{-\infty}^{\infty}(S_0\beta/2)(\nu - \alpha)^2\exp(-\beta|\nu - \alpha|)\,d\nu = (2/\beta^2)S_0 \qquad (16)$$

The functional form (15) is known as the Laplace distribution.

The absorption spectrum is $\nu|\epsilon(\nu)|^2$, $\nu > 0$. The emission spectrum is $\nu^4|\epsilon(\nu)|^2$, $\nu < 0$. We now write the emission spectrum as a function of a positive frequency variable. Because $\alpha > 0$, we have

$$I(\nu) \equiv \nu^4|\epsilon(-\nu)|^2 = (S_0\beta\exp(-\beta\alpha)/2)\nu^4\exp(-\beta\nu) \qquad (17)$$

This is a functional form that fits closely the results of the simulations, as shown in Figure 6.

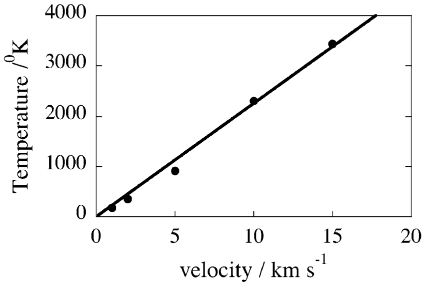

Figure 7. Radiation temperature of the hot cluster vs the impact velocity, points. The dashed line is a fit to a linear dependence.

Figure 7 shows the temperature T, $\beta = h/k_BT$, vs the impact velocity. The finite value of the parameter α is what ensures that the first oscillator sum is finite. α has the dimensions of frequency so that $h\alpha/k_B$ has the dimensions of temperature. But $h\alpha/k_B$ is significantly smaller than the temperature T. This is because α is entirely quantal in origin.

Discussion

The hot cluster has been shown to be characterized by two temperatures. One is the translational temperature that characterizes the random kinetic energy distribution of the atoms during the later stages of the compression and after the cluster fragments. The impact very effectively converts a very high fraction of the initially directed kinetic energy, the energy of the center of mass motion during the approach to the surface, to random kinetic energy. Therefore, the translational temperature scales linearly with the energy of impact. The second temperature is that characterizing the electronic deformation of the colliding atoms during the later stages of the compression of the cluster. This temperature is measured by the spectral width of the spectrum. The spectral width of collision-induced spectra scales as the impact velocity. Therefore, the electronic temperature that we compute scales linearly with the velocity of impact. For hypersonic impact the electronic temperature is high compared to room temperature but is significantly lower than the translational temperature. There may also be a collision-induced spectra when the cluster atoms collide with the surface. We here assumed that this contribution is quenched by the surface.[38]

The inequality of the two temperatures is only to be expected. The simulations presented in this paper constrain the electronic state of the cluster to remain as the ground state. We use the Born−Oppenheimer approximation meaning that we equilibrate the electrons at each stationary configuration of the cluster. We do not allow the electrons to equilibrate with the fast moving nuclei. We will try to lift this restriction in our future work. This will further broaden the spectrum because electronic transitions will become possible. But what we have shown is that even without electronic excitation there can be observable emission induced by the fast relative motion of the atoms in the hot cluster.

The collision-induced emission lasts only as long as the cluster is dense enough that atoms collide. Because the hot cluster fragments soon after the impact, the photons are emitted only during a brief time interval. The experimental detection of the emission will, therefore, probably require gating of the detector.[39] It remains to be seen if the bright flash of light that is radiated from violent explosions has a collision-induced origin, but it too lasts for only a very short while.

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(9) As is well-known, the spectrum can be computed from the dipole or the dipole velocity or the dipole acceleration. For exact wave functions these three formulations are strictly equivalent. Quantum chemists are familiar with the observation that for approximate electronic wave functions the three ways do not give identical results. Here we make the same observation for the nuclear motion. The spectrum that we compute from the dipole is qualitatively similar to that computed using the dipole velocity, with one essential difference. The spectrum computed from the dipole velocity will be an asymmetric function of frequency and as such will have a small but finite first moment. The spectrum computed from the dipole will be a symmetric function of the frequency and its first moment vanishes identically. See ref 8 for a further discussion.

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(39) We are indebted to Prof. A. H. Zewail for this observation.