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Calculated spectrum for near-dissociation H_3^+: a first attempt

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Discrete variable representation (DVR) calculations are performed for H_3^+. These calculations yield rotation–vibration wavefunctions which extend all the way to dissociation for the ground ($J = 0$) and first two ($J = 1, 2$) rotationally excited states of the system. Approximately 10 million linestrengths are computed for transitions involving these states and infrared spectra in the near-dissociation region are synthesized. These spectra are analysed and the steps necessary to obtain a theoretical version of the Carrington–Kennedy (1984, *J. chem. Phys.*, **81**, 91) infrared H_3^+ photodissociation spectrum are discussed.

1. Introduction

More than a decade ago Carrington and co-workers [1] recorded a remarkable spectrum produced by the simplest of triatomic molecules, H_3^+. In a very small window (only 222 cm^{-1}) of the infrared photodissociation spectrum they observed some 27 000 transitions which showed no signs of any structure, and little hope of understanding. When viewed under low resolution the spectrum shows a coarse grained structure [2, 3] which has been the subject of much (semi-)classical [4–11] and some quantal [12–15] analysis. The spectrum comprises transitions between the high energy vibrational states of the rotating molecule close to the dissociation limit. Almost no work has been done on the spectroscopy of polyatomic molecules at this limit.

In this paper we present a first attempt at actually synthesizing infrared spectra of H_3^+ in the near dissociation region. Although such treatments are relatively straightforward for van der Waals molecules (e.g., [16]), this is to our knowledge the first time a chemically bound, polyatomic molecule has been studied in this fashion.

2. Calculations

2.1. $J = 0$

We performed calculations for the vibrational states of H_3^+, i.e., those with zero rotational angular momentum (J), using a discrete variable representation (DVR) based method some years ago [17]. There was some dispute over the accuracy of these results [18] which led to us revising our procedure somewhat [19]. More recently Bramley *et al.* [20] have obtained very accurate energy levels (but no wavefunctions) for this problem.

The present $J = 0$ calculations are based on our revised results. They were performed using the correct MBB potential [21], program DVR3DRJ [22] and

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scattering coordinates. As has been discussed elsewhere [19] scattering coordinates do not give the full symmetry for H_3^+. However for our purposes it was sufficient to consider only the odd-parity block containing states of E and A_2 symmetry as the A_1 symmetry states given by the even-parity block are forbidden due to nuclear spin considerations.

The calculations used previously optimized [19] parameters for the basis functions associated with each coordinate. However, for this work we chose to diagonalize a larger final Hamiltonian of dimension 10 000 rather than the 8 500 dimensional one diagonalized previously. Comparison with the excellently converged results of Bramley *et al.* [20] suggest that, for all except the last few levels below dissociation, our results are converged to 1 cm^{-1} or better. For the last few states some are up to 4 cm^{-1} in error. Our analysis suggests that further increases in the dimension of the final Hamiltonian would be unhelpful without a corresponding increase in the number of DVR grid points used in the calculation.

This calculation used a total of 55 CPU hours and almost a gigabyte of memory on a Convex C3860 at the University of London Computer Centre. Of this 44 h was spent diagonalizing the final $10\,000 \times 10\,000$ matrix using the NAG routine F02ABF [23]. 1000 eigenvectors, which extends somewhat above dissociation, were saved for future use.

2.2. *J = 1 and 2*

Calculations were performed for the lowest two rotationally excited states, $J = 1$ and $J = 2$, utilizing the DVR adaptation of the two-step method tested previously [24]. These calculations used program DVR3DRJ for the first step and ROTLEV3 for the second [22].

The body-fixed z-axis was taken parallel to the diatom axis in atom–diatom scattering coordinates [24]. As a consequence it was necessary to consider both even- and odd-parity blocks in calculations with $J > 0$. However in each case it was necessary to compute only one of the two Wang symmetries. If the rotational parity is given by $(-1)^{J+p}$ with $p = 0$ or 1, then the A_2 and E symmetry states are given by the $J = 1$ odd $p = 1$, $J = 1$ even $p = 0$, $J = 2$ even $p = 1$ and $J = 2$ odd $p = 0$ calculations. Only these calculations were attempted.

The first 'vibrational' step of the calculations used the same number of DVR points in each coordinate as the $J = 0$ study. The same basis set parameters were also employed, except in the case of the spherical oscillator functions for the atom–diatom coordinate, where $\alpha = 0$ was used for the $J > 0$ calculations [24]. In this step of the calculation it is assumed that k, the projection of J onto the body-fixed z-axis is conserved. Calculations similar in character to the $J = 0$ calculation described above are performed for each k from p to J. In each case a final Hamiltonian matrix of size 10 000 was diagonalized and the 2200 lowest solutions retrained for the second step. The calculation requiring the most CPU time for this step was the $J = 2$ odd $p = 0$ calculation which used almost 150 h.

The second step in the calculation introduces Coriolis-coupling between k blocks. This step was not necessary for the $J = 1$ odd $p = 1$ calculation for which there is only one k block. For this block 1000 first step eigenvectors were retained for calculating transition intensities.

The $J = 1$ even $p = 0$ and $J = 2$ calculations were performed using program ROTLEV3 [22, 24]. Because a comparatively large number of solutions were required from these calculations the (sometimes more efficient) iterative diagonalization procedure usually used in ROTLEV3 was replaced by the standard symmetric Hamiltonian diagonalizer F02ABF [23]. These calculations all used 4000 eigenvectors from the first step, chosen using energy ordering, to provide a basis for the second step. 1500 eigenvectors were saved for the calculations ($J = 1$ even $p = 0$ and $J = 2$ even $p = 1$) comprising two k blocks and 2000 eigenvectors for the three k blocks, $J = 2$ odd $p = 0$ calculation. In all cases these were sufficient to extend above dissociation. The calculations took between 15 and 18 h CPU time each.

We could not afford to perform an extensive set of calculations with different parameters to assess the convergence of these calculations, although a number of calculations were performed using up to 6000 first step eigenvectors in ROTLEV3. We can estimate that our error in the first step is similar to, or possibly slightly worse than, that quoted for the $J = 0$ calculations above. The error in the second step was generally rather smaller than this, perhaps about 0•2 cm^{-1}, except for the $J = 2$ odd $p = 0$ calculation which gave some states in error by $\sim 1\ \mathrm{cm}^{-1}$.

2.3. *Dipole calculations*

The DVR based program DIPOLE3 [22, 25] was used to calculate transition linestrengths for *all* transitions allowed by the rigorous dipole selection rules

$$\Delta J = 0,\ \Delta p = \pm 1 \quad \text{or} \quad \Delta J = \pm 1,\ \Delta p = 0. \tag{1}$$

This gives five possible blocks of transitions. $\Delta J = 0$ (Q-branch) transitions are given by $J = 1$ even $p = 0 \leftrightarrow J = 1$ odd $p = 1$ and $J = 2$ even $p = 1 \leftrightarrow J = 2$ even $p = 0$. $\Delta J = \pm 1$ (P- or R-branch) transitions are given by $J = 0$ odd $p = 0 \leftrightarrow J = 1$ even $p = 0$, $J = 1$ odd $p = 1 \leftrightarrow J = 2$ even $p = 1$ and $J = 1$ even $p = 0 \leftrightarrow J = 2$ odd $p = 0$.

As the $J = 0$ calculations used a different DVR grid for the atom–diatom coordinate to the $J > 0$ calculations, it was necessary to transform the eigenvectors from this calculation onto the same DVR grid as the $J = 1$ even $p = 0$ calculation. This was done by using an intermediate transformation via a finite basis representation (FBR) in this coordinate.

The *ab initio* dipole surfaces of MBB [26] were used in program DIPOLE3 [22] to compute all the transitions within the five allowed blocks. The largest of these calculations ($J = 1$ even $p = 0 \leftrightarrow J = 2$ odd $p = 0$) used 98 h of CPU time and about a gigabyte of memory. In practice the elapsed times for the DIPOLE3 calculations were shorter than this because this program was efficiently parallelized by the Convex FORTRAN compiler, using up to 550% of 6 CPUs when available. In all just over 10 million linestrengths were computed and stored for spectral analysis, although it should be noted that many of these transitions involve states lying above the dissociation limit.

2.4. *Spectral analysis*

In order to synthesize spectra in the near dissociation region, it was decided to work within a model whereby transitions into a certain energy window were analysed. Furthermore, as we have a very large number of transitions, no attempt was made to analyse individual transitions. Instead we gave each transition a Gaussian profile of width 4 cm^{-1}, similar to the method used by Carrington and co-workers to construct their coarse grained spectrum [2, 3]. The resulting intensity was binned in boxes of width 1 cm^{-1} for plotting.

Spectra with transition frequencies, ω, between 0 and 2000 cm^{-1} were analysed using various models. A number of different methods of selecting energy windows were tested; in the end we settled on one where only (absorption) transitions to states in an energy window of width ΔE were retained in our spectrum. This model was chosen so that energy windows of arbitrary size did not favour transitions of a particular frequency and so we could ensure that, for a particular spectrum, transitions were only to states below/above dissociation as required. Spectra were generated which (a) included all transitions to the given energy window and (b) only included the strongest transitions with a linestrength greater than S. Carrington and Kennedy found that analysing only the strongest of their transitions served to accentuate the coarse grained structure in their spectrum. Using $S = 0{\cdot}08\ \mathrm{D}^2$ meant that typically less than 2% of the transitions were retained in the spectral synthesis (D = debye $\approx 3{\cdot}335\,64 \times 10^{-30}$ C m).

3. Results

3.1. *Density of states*

Before turning to synthetic spectra it is worth commenting briefly on our observed density of states for the rotational calculations. Berblinger *et al.* [27] compared quantal and semi-classical densities of states for the vibrational ($J = 0$) states of H_3^+. Their results showed excellent agreement between the results of full quantal calculations and densities obtained by numerically computing the volume of phase space.

Berblinger and Schlier [28] extended their semi-classical calculations to cases where $J > 0$. They computed the ratio

$$R_J(E) = \frac{\rho_J(E)}{(2J+1)\,\rho_0(E)}, \tag{2}$$

where $\rho_J(E)$ is the density of states with rotational angular momentum J at excitation energy E. They found that the ratio R was essentially constant with energy and in general was slightly less than unity. For example their R_2 has a value of 0•91.

Figure 1 compares our density of states as a function of energy for $J = 0$ and $J = 2$. It can be seen that the curve for $0{\cdot}91 \times 5 \times \rho_0$ curve passes directly through the ρ_2 curve. Thus the quantal and semi-classical estimates of the density of states are again in excellent agreement. Similar agreement was found for our $J = 1$ calculations.

These comparisons provide independent confirmation of the convergence of our results. In part the closeness of the agreement is due to use of the same potential for both calculations. Of course the MBB potential is not the true potential. In particular it lacks any representation of the long range attractive terms which should dominate near dissociation. Such terms would undoubtedly increase the density of states.

3.2. *Spectra*

Sample spectra for transitions to a 33 000•0–35 035•2 cm^{-1} energy window, where 35 035•2 cm^{-1} was taken to be the dissociation energy of the system [29], are shown in figures 2 and 3. These spectra combine P-, Q- and R-branch transitions although, as discussed below, each branch was also analysed separately. Although we synthesized infrared spectra between 0 and 2000 cm^{-1}, the figures given concentrate on the 400–1200 cm^{-1} region.

The only coherent explanation for the structure observed in the H_3^+ infrared photodissociation spectrum has been offered by Gomez-Llorente and Pollak [5]. These

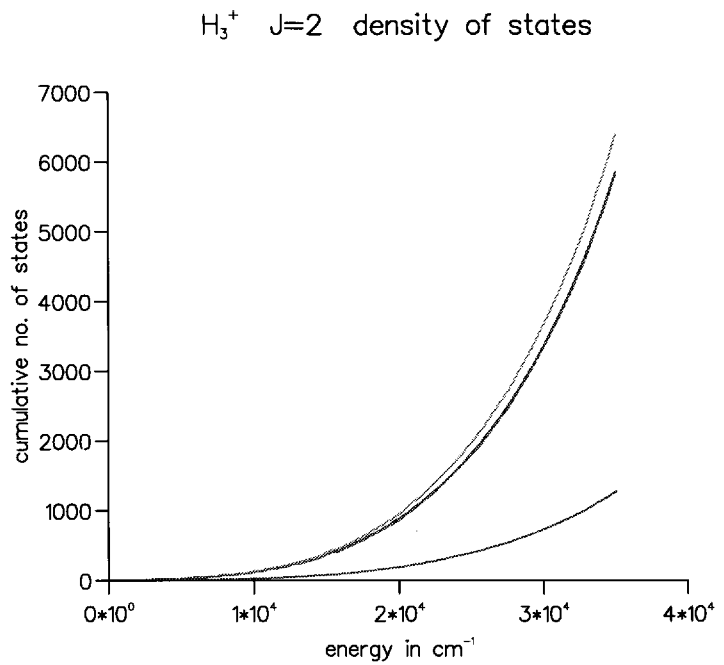

Figure 1. Cumulative number of H_3^+ energy levels as a function of energy up to dissociation. The lowest curve is for $J = 0$. The top curve is 5 times the $J = 0$ curve. The middle two curves, which are indistinguishable on this scale, are for $J = 2$, and $0{\cdot}91 \times 5$ times the $J = 0$ curve.

workers suggested that the peaks were part of an R-branch of a mode whose band origin was in the 600 cm^{-1} region. In this explanation the clumps are due to the R(5)–R(8) transitions and thus should not be reproducible by our calculations which only consider rotational levels up to $J = 2$. However our calculation should give the R(0) and R(1) transitions, the corresponding P-branch and any possible Q-branch transitions of this mode. We therefore analysed the spectrum in the 400–800 cm^{-1} region where these features should lie, as well as the 800–1200 cm^{-1} range which actually covers the frequencies used by Carrington and Kennedy in their experiments.

The characteristic feature of the Carrington–Kennedy spectrum is a series of broad peaks separated by approximately 50 cm^{-1}. Following Gomez-Llorente and Pollak's 'assignment', one might expect to see a similar series comprising P(1), P(2), R(0) and R(1) features and with a $\sim$ 100 cm^{-1} gap (or a Q-branch) centred on the band origin at $\sim$ 600 cm^{-1}. Figure 2 shows spectra for this region.

It is possible to convince oneself that such a series exists, especially for the spectrum synthesized using the strongest transitions (figure 2(*b*)), with peaks centred at approximately 450, 500, 600 and 650 cm^{-1}. This identification, however, should be treated with great caution. The strongest peaks in the spectrum do not contribute to this structure which cannot be readily identified in the spectrum containing all transitions. More significant is our analysis of the separate branches. These show that the largest flux, and some of the structure identified above, lies in the Q-branch while neither 'P-branch features' (at 400 and 450 cm^{-1}) nor the 'R-branch features' (at 600 and 650 cm^{-1}) can be identified with the P- or R-branch spectrum respectively.

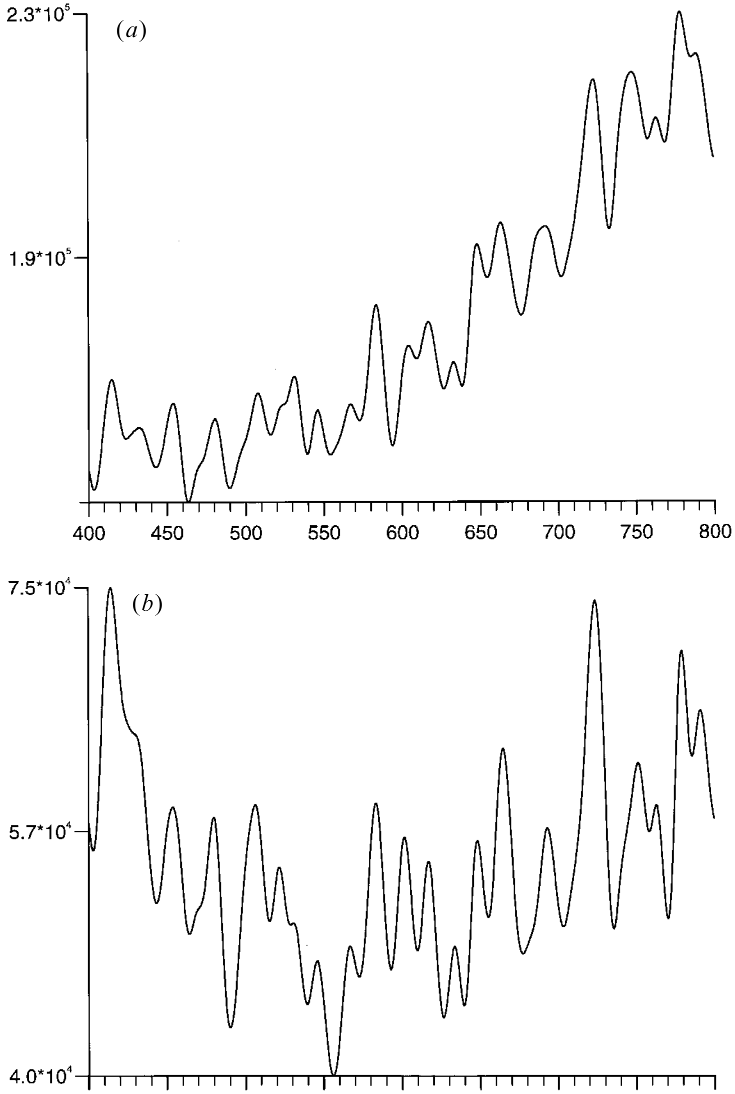

Figure 2. H_3^+ spectrum at infrared frequencies of 400–800 cm^{-1} in arbitrary intensity units. The spectrum was synthesized using all transitions of the relevant frequency into the 33 000•0–35 035•2 cm^{-1} energy window. All transitions were given a natural width of 4 cm^{-1} and binned into boxes of width 1 cm^{-1}: (*a*) includes all transitions and (*b*) includes transitions with linestrength greater than 0•08 D^2 only.

Figure 3 covers the frequency region analysed by Carrington and Kennedy. Here it is possible to identify a series of broad features in the 950–1150 cm^{-1} region. These features are particularly prominent in the strongest transitions spectrum, figure 3 (*b*), but are matched by features in the full spectrum. However it should be noted that these features are separated by $\sim$ 70 cm^{-1}, which is significantly more than 50 cm^{-1}. Furthermore these features are a mixture of P-, Q- and R-branch transitions suggesting that their prominence may be an accidental feature of the present calculations rather than a manifestation of any underlying structure.

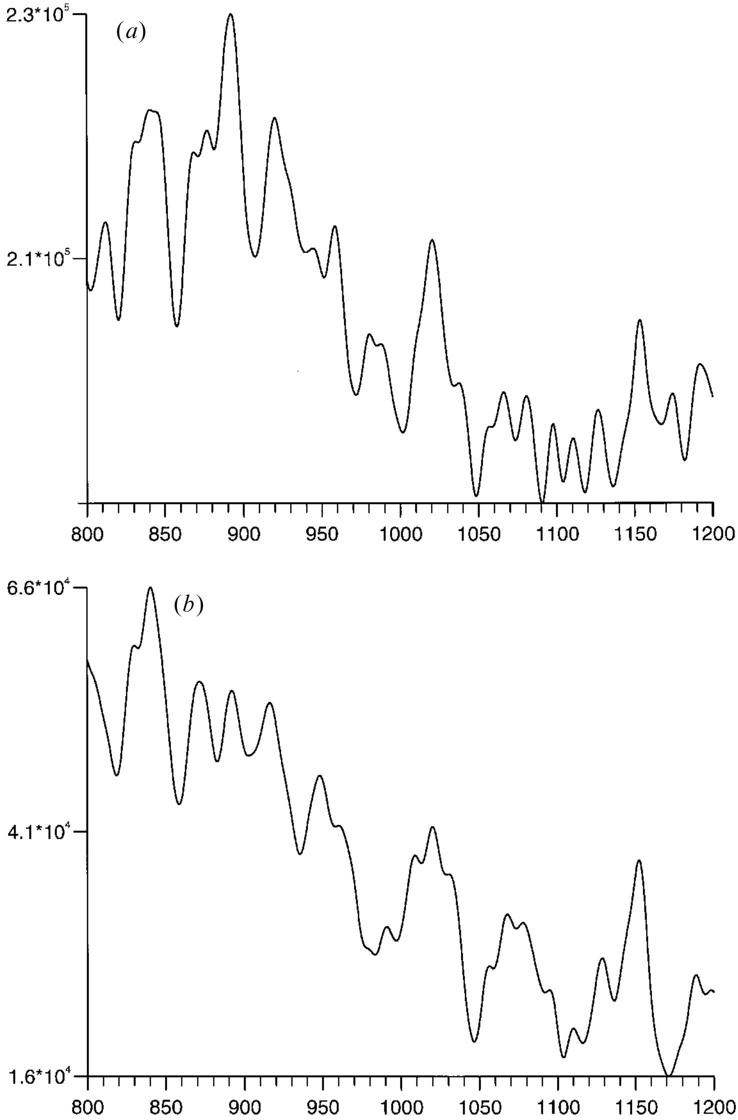

Figure 3. H_3^+ spectrum at infrared frequencies of 800–1200 cm^{-1} in arbitrary intensity units. The spectrum was synthesized using all transitions of the relevant frequency into the 33000–35035•2 cm^{-1} energy window. All transitions were given a natural width of 4 cm^{-1} and binned into boxes of width 1 cm^{-1}: (*a*) includes all transitions and (*b*) includes transitions with linestrength greater than 0•08 D^2 only.

Figure 4 covers the frequency region analysed by Carrington and Kennedy at energies just above dissociation. To restrict our analysis to states which can be trapped behind angular momentum barriers, this spectrum is generated using a significantly smaller energy window; only final energies in the range 35035•2–35100•0 cm^{-1} were selected. One consequence of this is to lower the number of transitions considered leading, particularly in the spectrum generated using the strongest transitions (figure 4(*b*)), to pronounced structures in our synthetic spectrum.

Again it is possible to identify possible broad features in figure 4. However none of

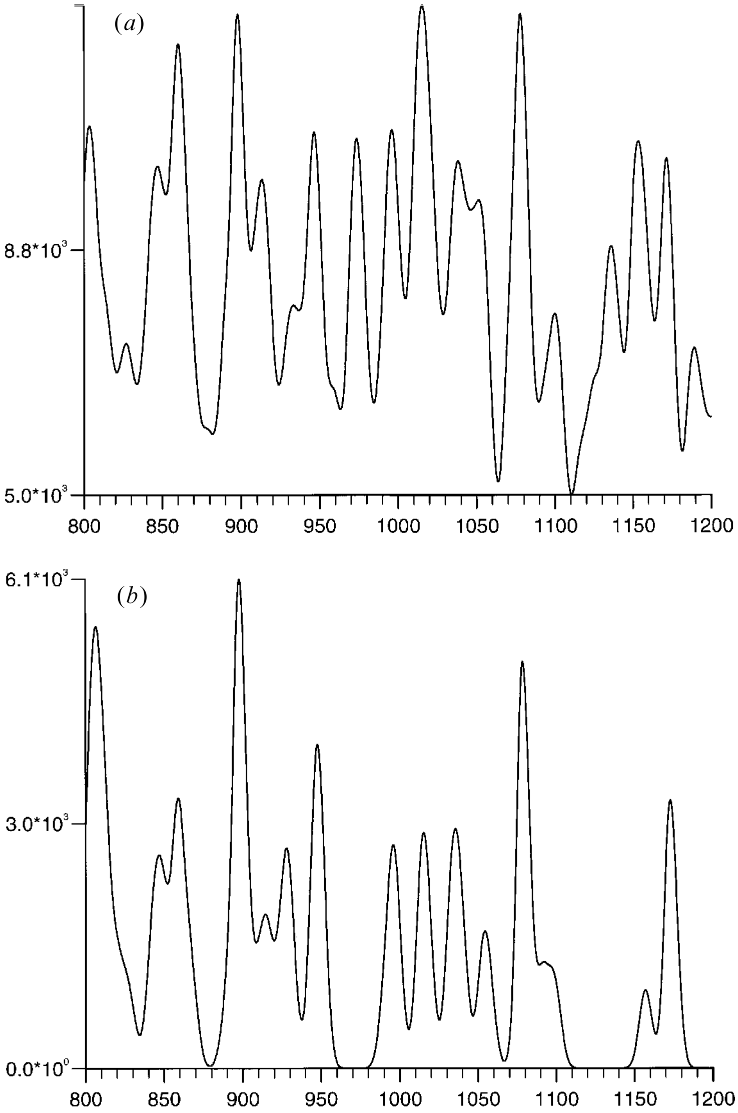

Figure 4. H_3^+ spectrum at infrared frequencies of 800–1200 cm^{-1} in arbitrary intensity units. The spectrum was synthesized using all transitions of the relevant frequency into the 35 035·1–31 000·0 cm^{-1} energy window. All transitions were given a natural width of 4 cm^{-1} and binned into boxes of width 1 cm^{-1}: (*a*) includes all transitions and (*b*) includes transitions with linestrength greater than 0·08 D^2 only.

the structures are particularly close to those obtained by Carrington and Kennedy. Perhaps this is not too surprising in view of deficiencies of the present calculation which we discuss below.

4. Discussion

The calculations presented here are very much a preliminary attempt at reproducing the photodissociation spectrum of Carrington and Kennedy. As such it is probably not surprising that we have been unable to make any definite analogy between our synthetic spectra and those observed in the photodissociation experiment. It is however worth considering what aspects of the calculation would need to be improved before a more definitive attack on the problem can be performed.

There are probably four problems with the present calculations that need to be addressed. We suspect that the least important of these is the reliability of the present results for the given model. Although there is undoubtedly room for improvement in the solutions to the problem as solved here, we would be surprised if such improvements made any qualitative change to the spectra synthesized here.

In general the accuracy of a rotation–vibration calculation such as this is largely determined by the accuracy of the potential energy surface used in such a calculation. The MBB potential [26] used here performs very well in the region about the H_3^+ minimum but was not designed for calculations probing the region more than 25 000 cm^{-1} above equilibrium. One therefore has to be mindful that the potential energy surface may be wholely unreliable at dissociation; in particular we have already noted the absence of attractive long range terms in the analytic form of the potential. However test show that the surface does in fact behave in a physically reasonable fashion at the dissociation limit.

All the previous classical, semi-classical and quantal studies on this system have used either the MBB potential or ones which are even cruder. So far there has been no suggestion that any of the properties of the system identified in these studies are dependent on the choice of a particular potential; something that has been tested on several occasions [13, 29–31]. In particular the semi-classical predictions of Gomez-Llorente and Pollak [5], with which we are particularly concerned here, were made using the DIM potential of Preston and Tully [33]. Subsequent semi-classical calculations using the MBB potential showed the same features with only minor numerical differences [30, 31]. Indeed test calculations have shown that a potential constructed as the sum of Morse potentials in the three atom–atom distances reproduces the important features of previous (semi-)classical calculations on H_3^+ [13].

In the absence of a high quality global potential there is little more one can say on this topic except the major improvements in *ab initio* potentials, such as [32], in the region of the minimum mean that an attack on the global H_3^+ problem would be very worthwhile and is easily within the range of present methods.

One aspect of the MBB surface that concerned us in particular is its actual behaviour at dissociation. It should be noted that the analysis of Gomez-Llorente and Pollak [5], which we have also used, is very much based on a model of H_3^+ rotating like a diatomic with a single rotational constant. Furthermore the observed constant is very close to that of molecular hydrogen which of course is a product at the dissociation limit we are analysing. An important question is therefore whether the MBB surface gives H_2 with the correct rotational constant at dissociation. Tests on the surface showed that it gives H_2 with an equilibrium geometry of 1•435 a_0 and hence a rotational constant some 5% smaller than the true value. This difference, though important for any accurate work, is probably not significant in the context of the present calculations.

Another important aspect of the present calculations is that they are mostly confined to truly bound states of the ion. Although it is possible that the structure of the levels changes dramatically at dissociation, there is another probably more important aspect to this. Above the dissociation limit, the now quasibound states each have a lifetime which is likely to vary strongly with the nature of the states in question, this is certainly true of classical trajectories in this energy region [34]. The measurements of Carrington and co-workers are heavily moderated by lifetime effects. In practice only transitions involving states which satisfy certain constraints on their lifetimes can contribute to their observed photodissociation spectra. This means that the experiment is sensitive to only a portion of the transitions studied here. In other words, any attempt to calculate the Carrington and Kennedy photodissociation spectrum requires the experiment to be modelled, particularly for lifetime effects, and not just the spectra near dissociation to be analysed in some impartial fashion. This task remains difficult but may be achievable with current techniques (e.g. [35]).

The subject of what rotational levels are being monitored in the photodissociation experiment has been debated by people performing classical calculations [7, 9–11]. However it is clear that the level of rotational excitation in the present calculations is inadequate. There is no problem, in principle, in increasing the level of excitation treated, indeed the H_3^+ system has been treated at very high J in the dissociation region [29]. Such calculations are computationally expensive and could not be contemplated on the computer facility used for the current work.

In conclusion, we have performed calculations which give energy levels and wavefunctions for all the bound states of H_3^+ with two or less quanta of rotational angular momentum. These calculations have been used to compute synthetic spectra in the near-dissociation region as a first step in a direct fully quantal attack on the infrared H_3^+ photodissociation spectra of Carrington and co-workers [1–3]. It should be noted that our database of some 10 million transitions contains information on other aspects of the spectroscopy of H_3^+. Thus, for example, more approximate calculations studying vibrational band intensities have predicted a pronounced structure in the near-infrared and optical spectroscopy of H_3^+ [36]; this and other questions can be explored using the linestrengths generated in the course of this work.

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